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FATE AND EFFECTS OF TRACE ELEMENTS IN SEWAGE SLUDGE WHEN APPLIED TO AGRICULTURAL LANDS

A LITERATURE REVIEW STUDY

CALIFORNIA UNIVERSITY

PREPARED FOR
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16. Abstracts Uses of As, Ba, B, Cd, Cr, Co, Cu, Pb, Mn, Hg, Mo, Ni, Se, Ag, Sn, V, and Zn are reviewed. Total concentrations of trace elements in sewage sludges vary widely. Ranges are reported for sludges from approximately 300 treatment plants from different regions in the U.S.A., Canada, Sweden, England, and Wales. No apparent relationship exists between the total concentration of trace elements in sludge and the amount dissolved by organic acids or water. Field and greenhouse studies have demonstrated that yields and trace element concentrations of higher plants grown on sludge-amended soils are dependent upon the amount of sludge applied, trace element composition of the sludge, soil pH, and plant species. In most soils the percentage of Ag, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sn, and Zn applied in the form of sludge which moves beyond the depth of tillage is quite small. Mobility of Mo, As, and Se is normally limited. Boron is mobile in most soils. Application of most sludges at a rate of 400 m. tons/ha if mixed uniformly throughout the surface 15 cm will add more Cd, Cu, Hg, and Zn than is normally present in natural soils. 107 references.

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

> studies on the effects of environmental contaminants on man and the biosphere, and
>
> a search for ways to prevent contamination and to recycle valuable resources.

This review was prepared for the Ultimate Disposal Section of the Advanced Waste Treatment Research Laboratory to help evaluate one of the potential hazards associated with the disposal of pollutants removed from water. All forms of pollution control create their own risk of causing pollution in another area. Only by carefully weighing the benefits of a disposal technique against the corresponding risk can we make a rational choice between alternatives.

A. W. Breidenbach, Ph.D.
Director
National Environmental
Research Center, Cincinnati

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I. INTRODUCTION

One of the most pressing problems facing metropolitan areas today is disposal of large volumes of liquid and solid wastes generated by urban and industrial activities. The need to conserve and re-use water, problems associated with water pollution resulting from discharging wastes into surface waters, air pollution resulting from the incineration of the waste, and the scarcity of suitable sites for landfill operations have prompted municipalities and other governmental agencies to investigate alternative means of disposal. One alternative disposal operation which is currently receiving rather widespread attention is the disposal of wastes onto agricultural land.

The practice of spreading urban wastes onto agricultural land is not new, and has been used on a limited scale for decades. Sewage treatment plant effluents and sewage sludges are currently and have for many years been used to irrigate field crops and recreation areas such as parks and golf courses. The settleable solids from sewage treatment plant works are processed and sold as soil amendments and low grade fertilizers. Composted sludge and composts consisting of garbage with or without the addition of sewage sludge also are produced and marketed. Law (1968) recently reviewed the literature on the agricultural utilization of sewage effluent and sludge and cited 284 references on the subject.

Although there has been a long history of research on the use of sewage on agricultural land, these works have been primarily concerned with the fertilizing value of materials and their effects on crop yields.

There have been very few studies designed to evaluate the long-term consequences of applying sewage treatment plant wastes on land. One of the potential problems associated with the long-term (decades) applications is the accumulation of toxic concentrations of trace elements. The present study will attempt to evaluate this question based upon the published information available.

The term "trace element" is rather loosely used in the literature to designate a number of elements which occur in natural systems in

small concentrations. As defined in many dictionaries, trace elements are those chemical elements, especially metals, used by organisms in minute quantities but believed essential to their physiology. However, the term is and has been used to designate elements with no known physiological function. With the recent widespread concern over the quality of the environment, the term has been used to refer to elements which are, when present in sufficient concentrations, toxic to living systems. Other terms which have been used, and which for all practical purposes can be considered synonyms for the term "trace elements" are "trace metals," "trace inorganics," "heavy metals," "micronutrients," and "microelements." The use of the term "micronutrient" usually has been restricted to those trace elements known to be essential for the growth of higher plants, e.g. Cu, Zn, Mo, B, Mn, and Fe. The use of the term "heavy metals" in the literature is usually, but not always, restricted to those metals which have densities greater than 5.0. In the present paper, the elements in sewage sludges considered will be molybdenum (Mo), manganese (Mn), barium (Ba), copper (Cu), zinc (Zn), nickel (Ni), cadmium (Cd), cobalt (Co), tin (Sn), chromium (Cr), lead (Pb), vanadium (V), boron (B), mercury (Hg), arsenic (As), selenium (Se), and silver (Ag) and are for convenience referred to as trace elements.

Over the past decade or so, interest in trace elements in the environment has been rather extensive due principally to discoveries linking them directly or indirectly with adverse effects on human and animal health and concomitant observations of excessive trace element pollution of air, land, and water caused principally by urban and industrial activities. The extensive research of H. A. Schroeder and his co-workers at the Dartmouth Medical School serves to illustrate the current interest of medical researchers in trace elements (see references cited by Lisk, 1972). A number of reviews have been published recently on trace element research (Lisk, 1972; Allaway, 1968; Lagerwerff, 1972; Hodgson, 1963; Antonovics, Bradshaw, and Turner, 1971; and Bowen, 1966).

II. RESULTS OF PUBLISHED REPORTS

Sources of Trace Elements Found in Sewage Sludges

Trace element concentrations in sewage sludges are related to the kinds and amounts of urban and industrial discharges into the sewage treatment systems and to the amounts added in the conveyance and treatment systems. The composition of urban and industrial waste changes as consumer products, industrial processes, and industrial activity change, so sewage sludges may vary in their chemical composition from time to time. Since the sources of municipal refuse and sewage are the disposal of consumer and industrial products as well as disposal of materials used in their production, the trace elements composition of wastes will depend upon uses of trace elements. For this reason, a brief review of uses of trace elements is presented in the following section.

Uses of Trace Elements

Uses of As, Ba, B, Cd, Co, Cu, Pb, Cr, Mn, Hg, Mo, Ni, Se, Ag, Sn, V, and Zn and their compounds have been extensively reviewed in various reports (Miner, 1969; Athanassiadis, 1969a, 1969b; Sullivan, 1969a, 1969b, 1969c, 1969d, 1969e; Stahl, 1969a, 1969b; and U. S. Bureau of Mines, 1971). A summary of findings, by element, follows:

Arsenic. Most forms of arsenic are highly toxic and its compounds are used in insecticides, rodenticide, fungicides, and herbicides. Compounds of As are used in the manufacture of glass, enamels, ceramics, oil cloth, linoleum, and electrical semiconductors and photoconductors. They are also used as pigments in painting, in fireworks to give an intense white flame, as wood preservatives, and in the textile and tanning industries. It is also used in making certain types of bronzes and other varieties of alloys.

Barium. Barium metal is used as a getter in electronic tubes and as an alloying agent with Ni for spark plug elements. Its compounds are used as mordants for printing fabrics and acid dyes, in weighting and dying textile fabrics, in bleaching, electroplating, synthetic

rubber vulcanization, lubricants, pesticides, corrosion inhibitors, pigments, photocells, semiconductors, dielectric and magnetic amplifiers, computer elements and memory devices. They are also used in the manufacture of paper, glass, and case hardened steels and matches. Organometallic compounds of Ba are added in amounts ranging from 0.075-0.20 percent by weight to diesel fuels as a black smoke suppressant.

Boron. The principal source of boron in most sewage is the household use of boron-containing soaps, detergents, and cleaners. Compounds of boron are used in the manufacture of glazes, cements, crockery, porcelain, enamels, glasses, alloys, semiconductors, lubricants and hardened steels. Boron compounds are also used as agricultural fertilizers, rubber vulcanizers, anesthetics, for fireproofing and weatherproofing wood and fabrics, in the leather and tanning industry, in printing and dying, paints, photography, and solder.

Cadmium. Principal uses of Cd are in electroplating, pigments and chemicals, and alloys. Household appliances (vacuum cleaners, refrigerators, washing machines, television sets, radios, and stoves), automobiles and trucks, agricultural implements, and airplane parts, industrial machinery, hand tools (wrenches, pliers, screwdrivers) and fasteners of all kinds (nuts, bolts, screws, rivets, and nails) are commonly Cd coated. Compounds of Cd are rather extensively used as pigments, and as heat and light stabilizers in the plastics industry. Alloys of Cd are used in the production of bearings for aircraft and other internal combustion engines, for solders, and for low melting and brazing alloys. Recent uses of Cd are in the production of automobile radiators, and batteries. Sealed Cd batteries are used in many convenience appliances such as toothbrushes, electric shavers, flashlights, and knives. Cadmium is also used for luminescent dials, in photography, lithography, process engraving, rubber curing, and as fungicides.

Chromium. Consumption of Cr falls generally into the categories of the metallurgical, refractory, and chemical industries. Because of its chemical inertness and high melting point chromite ore is used in the manufacture of refractory bricks to line metallurgical furnaces.

Chromium metal is used in chrome steels and alloys for increasing the resistance and durability of metals. A number of metals are chrome plated and most communities have commercial facilities engaged in plating operations. Compounds of chromium are used in the dying and tanning industries, in the manufacture of inks, varnishes, glazes for porcelain, and as abrasives. Chromates also have a variety of applications as corrosion inhibitors; primer paints and dips for metals commonly contain chromates; soluble chromates are used as rust inhibitors in cooling towers, industrial coolers, air conditioning equipment, boilers of many types, and in certain metal pipelines. Chromates are also used in paper matches, some fireworks, and dry-cell batteries. Compounds of chromium are used as topical antiseptics and astringents, defoliants for certain crops, and in photographic emulsions as hardening agents.

Cobalt. Cobalt is used in the production of high grade steels, alloys, superalloys, and magnetic alloys. Cutting and other wear-resistant materials commonly are produced from Co steels and alloys. It is also used in smaller quantities as a drier in paints, varnishes, enamels, and inks, as a pigment, and as a glass decolorizer.

Copper. The principal uses of Cu are in the production of wire and brass. Copper is alloyed with Sn, Pb, Zn, Ni, Al, and Mn. It is widely used in electrical wires and other electrical apparatus. Because of its high thermal conductivity and comparative inertness copper is extensively used in containers such as boilers, steam pipes, automobile radiators, and cooking utensils. Copper tubing is widely used in water conveyance systems. It is also used in fungicides and fertilizers.

Lead. The two principal uses of Pb are in the production of storage batteries and the gasoline additives, tetraethyl and tetramethyl lead. With the more widespread use of non-leaded and low lead gasolines recently, amounts of lead used in gasoline have diminished slightly. In 1971 the average amount of Pb used in gasoline was 2.22 g per gallon, which compares with an average of 2.43 g per gallon used in 1970 (Ryan, 1971). Lead is also quite extensively used in ammunition, in the plumbing

industry as caulking compounds and solders in pigments, and as an anti-corrosive agent in exterior paints. Some Pb is still used in the production of insecticides.

Manganese. The principal uses of manganese are in the iron and steel industries. Manganese dioxide is used quite extensively in alkaline batteries, and in the glass, paints, and drying industries. Other compounds of manganese are used as driers for paints, varnishes, and oils, fertilizers, disinfectants, and as antiknock compounds for internal combustion engines.

Mercury. The major uses of mercury and its compounds are in electrical apparatus, electrolytic production of chlorine and caustic soda, in paints, industrial and control instruments, pharmaceuticals, and catalysts. Mercury is used in neon, fluorescent, and mercury-arc lamps, in silent switches, batteries, rectifiers, oscillators, and measuring instruments such as thermometers, barometers, manometers, hydrometers, and pyronometers. In the production of chlorine and caustic soda, it is used as a floating electrode in electrolysis. It is used in paints, floor waxes, furniture polishes, fabric softeners and laundry preparations to prevent mildewing and as an antifouling agent. It is also used as a fungicide in agriculture and the paper and pulp industry, and in antiseptics. As a catalyst, mercury is used in the manufacture of vinyl chloride and urethane.

Molybdenum. The largest single use of Mo is in the production of molybdenum steels and alloys. It is also used in pigments, filaments in lamps, electronic tubes, electric contacts and pigments. Molybdenum disulfide is used as a lubricant. Small amounts of Mo are used in fertilizers and as catalysts.

Nickel. Nickel is used primarily in the production of stainless and heat-resisting steels and steel alloys, in Ni-Cu or Cu-Ni alloys, other nickel alloys, and in electroplating. It is used in the production of storage batteries, magnets, electrical contacts and electrodes, spark plugs, machinery parts and as a catalyst for the hydrogenation of oils and other organic substances. Compounds of nickel are used as pigments in paints, lacquers, cellulose compounds, and cosmetics.

Selenium. Most of the Se consumed in the United States is used in the electronics and electrical industry. Rectifiers containing 0.5-25 g Se are used in electroplating, welding, battery charges, magnetic coils, arc lamps, and voltage regulators. Approximately the same amount of Se is used in the production of photoelectric cells which are used in light exposure meters, electric eyes, detectors, colorimeters, and pyrometers. Selenium is used with CdS to produce pigments referred to as lithophones. The pigments impart orange, red, and maroon colors to materials, and are used to color plastics, paints, enamels, inks, and rubber. It is also used in stainless steel and in photocopiers (Xerography). Selenium and its compounds are consumed in lesser amounts in such consumer goods as pharmaceuticals, deodorants, plastics, inks, oils (as an antioxidant), insecticides, parasiticides, bactericides, herbicides, fireproofing agents for textiles, insect repellants, glue, solid lubricants, and as paint and varnish removers. They are also used as accelerating and vulcanizing agents in rubber products, in medicines for animals, and as catalysts for oxidizing, dehydroginating, and hardening fats used in soaps, waxes, and edible fats.

Silver. Most silver which enters domestic and industrial waste water probably has as its source silver used in photographic materials. Silver is also used in electric contacts and conductors, electroplated ware, sterling ware, jewelry, and dental and medical supplies. It is also used in the production of mirrors, bearings, certain types of storage batteries, and as catalysts in certain industrial operations. Many low-melting brazes and solders contain silver.

Tin. In 1971 approximately 46 percent of the Sn consumed in the United States was used in the production of tin cans. Tin is used in the production of many alloys, babbitt, brass, and bronze and for galvanizing metals. It is also used in roofing materials, pipe and tubing, solder, and in collapsible tubes and foil.

Vanadium. The major uses of V are in vanadium steels and non-ferrous alloys. Vanadium compounds are used as catalysts in many industrial processes, as driers in paints and varnishes, as developers

in photography, mordants in drying and printing textiles, and in the production of colored glass and glazes.

Zinc. Zinc is used extensively as a protective coating on a number of metals to prevent corrosion and in alloys such as brass and bronze. Galvanized metals have a variety of applications in the building, transportation, and appliance industries. Galvanized pipes are commonly used in domestic water conveyance systems and zinc solubilized by corrosion is generally thought to make a substantial contribution to the Zn concentrations observed in waste waters. Zinc and its compounds are constituents of many household items including utensils, cosmetic and pharmaceutical powders and ointments, antiseptics and astringents, insecticide and fungicide formulations, glues, matches, inks, porcelain products, fabrics, and as a pigment in paints, varnishes, oil colors, linoleum, and rubber. Zinc and its compounds are used in the manufacture of parchment paper, phosphors for fluorescent and electric lights, glass, automobile tires, television screens, dry cell batteries, and electrical apparatus. They are also used as hardeners in cement and concrete, in printing, drying, and weighting textiles, and in agricultural fertilizers. A recent use of zinc which is increasing dramatically each year is in photosensitive copying paper.

Concentrations of Trace Elements Found in Sewage Sludges

The trace element composition of sewage sludges has been characterized relative to total concentration, organic acid extractable concentrations, and water-soluble concentrations. However, most of the data in the literature pertain to total concentrations.

Total Concentrations

The most complete assemblage of data on the chemical composition of sewage sludges are those reported by Berggren and Odén (1972), Berrow and Webber (1972), and Blakeslee (1973).

Berggren and Odén (1972) and Odén, Berggren, and Engvall (1970) have reported data for the concentration of trace elements in sewage sludges from many cities and towns in Sweden. A summary of the data of Berggren and Odén (1972) is presented in Table 1. The data show extremely large

Table 1--Contents of trace elements in sewage sludges from 93 treatment plants in Sweden[1/]

Element	Range	Mean	Median	No. Samples Within Ranges				
				1-10	10-100	100-1000	1000-10,000	>10,000
	----------μg/g----------							
Cd	2.3 - 171	12.7	6.7	67	24	2	0	0
Co	2.0 - 113	15.2	10.8	30	62	1	0	0
Cr	20 - 40,615	872	86	0	48	39	2	3
Cu	52 - 3300	791	560	0	1	69	23	0
Hg	<0.1 - 55	6.0	5.0	84	8	0	0	0
Mn	73 - 3861	517	386	0	1	82	10	
Ni	16 - 2120	121	51	0	65	26	2	0
Pb	52 - 2914	281	180	0	7	82	4	0
Zn	705 - 14,700	2055	1567	0	0	11	81	1

1/ Derived from data reported by Berggren and Oden (1972). The values reported are for the means of samples collected from 1968 through 1971.

variations in the chemical composition of the sludges from different treatment plants. Although mean values are reported in Table 1, they probably have little meaning since the means are highly influenced by a few abnormally high concentrations. For example, the concentration of Cr in most sludges falls in the range of 10-100 μg/g, but 3 of 93 samples had concentrations in excess of 10,000 μg/g. The median concentration and distribution of samples within ranges for the Swedish sludges are also presented in Table 1.

For comparison trace element concentration data for sludges from 57 treatment plants in Michigan, U.S.A., and for sludges from 42 treatment plants in England and Wales are presented in Tables 2 and 3. Again wide variation in concentrations occur from one treatment plant to another. Concentrations of Cd most commonly observed in sludges fall in the range of 1-10 μg/g. With Cr, the most common range usually falls within wider limits or from about 50-500 μg/g. Nickel commonly occurs in sludges at concentrations ranging from 20-200 μg/g, and Cu in the range of 100-1000 μg/g. The concentration of Zn in sewage sludges is consistently quite high and normally ranges between 1000-5000 μg/g. Median concentration, and the most common ranges for the sludges from Michigan, England and Wales, and Sweden are presented in Table 4. Except for Cr, variations which occur in concentrations of trace elements among the treatment plants in the three countries are reasonably comparable.

Berggren and Odén (1972) analyzed their data relative to the frequency with which trace elements occurred within certain concentration ranges. Extrapolating from their figures shows that approximately 80 percent of the sewage sludges from Sweden have trace element concentrations which fall within the following ranges (in μg/g dry matter): Zn (800-3200), Cu (200-1600), Pb (100-400), Mn (100-800), Cr (25-800) and Ni (25-600). Data from other locations (Tables 1, 2, 3, 5) suggest that concentration of most sewage sludges will fall within the ranges observed in Sweden. Odén, Berggren, and Engvall (1970) observed a linear log-log relationship between concentrations of Cd and Zn, Zn and Cu, Pb and Cu, and Ni and Cu in sewage

Table 2--Contents of trace elements in 57 sewage sludges from locations in Michigan, U.S.A.[1/]

Element	Range	Mean	Median	No. Samples Within Range				
				1-10	10-100	100-1000	1000-10,000	>10,000
	----------µg/g----------							
Hg	0.1 - 56	5.5	3.0	49	4	0	0	0
Cd	2 - 1100	74	12	28	20	8	1	0
Cr	22 - 30,000	2031	380	0	19	18	18	2
Cu	84 - 10,400	1024	700	0	1	42	13	1
As	1.6 - 18	7.8	7.5	48	9	0	0	0
Ni	12 - 2800	371	52	0	33	15	9	0
Pb	80 - 26,000	1380	480	0	2	43	10	2
Zn	72 - 16,400	3315	2200	0	1	9	44	3

1/ Derived from data reported by Blakeslee (1973).

Table 3--Contents of trace elements in 42 sewage sludges from locations in England and Wales[1/]

Element	Range	Mean	Median	No. Samples Within Ranges				
				1-10	10-100	100-1000	1000-10,000	>10,000
	----------μg/g----------							
Ag	5 - 150	32	20	11	30	1	0	0
B	15 - 1000	70	50	0	39	3	0	0
Ba	150 - 4000	1700	1500	0	0	7	35	0
Cd	<60 - 1500	<200	-	-	-	6	1	0
Co	2 - 260	24	12	19	22	1	0	0
Cr	40 - 8800	980	250	0	13	19	10	0
Cu	200 - 8000	970	800	0	0	33	9	0
Mn	150 - 2500	500	400	0	0	40	2	0
Mo	2 - 30	7	5	35	7	0	0	0
Ni	20 - 5300	510	80	0	26	12	4	0
Pb	120 - 3000	820	700	0	0	36	6	0
Sn	40 - 700	160	120	0	19	23	0	0
V	20 - 400	75	60	0	38	4	0	0
Zn	700 - 49,000	4100	3000	0	0	6	34	2

1/ From Berrow and Webber (1972).

Table 4--Comparison of median and range of trace element concentrations of sewage sludges from Michigan, USA; England and Wales; and Sweden[1/]

Element	Median Conc.			Most Common Range[2/]					
	USA (Michigan)	England and Wales	Sweden	USA (Michigan)		England and Wales		Sweden	
Cd	12	-	6.7	1-10	(49)	-		1-10	(72)
Cr	380	250	86	10-100	(33)	100-1000	(45)	10-100	(52)
Cu	700	800	560	100-1000	(74)	100-1000	(79)	100-1000	(74)
Ni	52	80	51	10-100	(58)	10-100	(50)	10-100	(70)
Pb	480	700	180	100-1000	(75)	100-1000	(85)	100-1000	(88)
Zn	2200	3000	1567	1000-10,000	(76)	1000-10,000	(81)	1000-10,000	(87)

1/ Data are from 57, 42, and 93 treatment plants in Michigan, England and Wales, and Sweden, respectively. For Michigan, England and Wales, and Sweden, data are derived from those published by Blakeslee (1973), Berrow and Webber (1972), and Berggren and Odén (1972), respectively.

2/ Percentage of samples within the concentration range indicated are given in parentheses.

sludges from Sweden. Their data show the following trace element ratios as common to most sewage sludges in Sweden: Cd:Zn (1:160), Zn:Cu (1:0.3), Pb:Cu (1:1.7), and Ni:Cu (1:5).

Less extensive data for trace element concentrations of sewage sludges from a number of locations in the U.S.A. and Canada are reported. These data have been compiled and are presented in Table 5. Generally speaking, the more recent data show concentrations which fall within the ranges previously discussed. The older data of Anderson (1955), however, show boron to be considerably lower, probably due to lesser use of boron in laundry products in 1955 than in recent years.

Data presented by Blakeslee (1973) are sufficiently extensive to make comparison of concentrations of trace elements in sewage sludges in relation to the type of treatment process. Ranges observed for undigested sludge, secondary digestor sludge, and vacuum filter cake sludge as reported by Blakeslee (1973) are presented in Table 6. The data show no consistent trends in trace element composition in relation to treatment process.

Organic Acid Soluble

British workers commonly use the concentration of trace elements extracted from soils with 0.5 N HOAc as an index of availability to higher plants. Consequently, Berrow and Webber (1972) determined the 0.5 N HOAc extractable trace element concentrations for a number of sewage sludges from England and Wales. Their data are reproduced in Table 7. Ranges of 0.5 N HOAc extractable trace elements from sewage sludges exceed ranges observed for soils (compare Table 7 with Table 17). Maximum amounts extracted for the sludges are considerably greater than maximum amounts extracted from soils. The percentages of the total content of trace elements in sludge which are extracted with 0.5 N HOAc vary quite markedly (Table 7). Patterson (1971) also evaluated amounts of 0.5 N HOAc extractable trace elements from sewage sludges. He presents data which show that percentages of trace elements extracted from sludges are not necessarily related to their concentrations. The wide variation in percentage 0.5 N HOAc extractable trace elements suggests that the chemical

Table 5--Concentrations or concentration ranges of trace elements in sewage sludges from various locations in the United States and Canada

Location	Element									Reference
	B	Cd	Cr	Cu	Ni	Mn	Mo	Pb	Zn	
	μg/g									
Athens, Ga.	9-18	-	-	350-530	11-37	123-268	-	-	1850-2850	King and Morris (1972a)
Columbus, Ohio	99-126	5.6-10.5	-	282-728	17-23	148-232	-	72-88	1605-1764	Miller (1973)
Dayton, Ohio	-	830	-	6020	<200	-	-	-	8390	Dotson (1973)
Cincinnati, Ohio	-	<40	-	4200	600	-	-	-	9000	Dotson (1973)
Chicago, Ill.	6-67	495	4200	385-1225	425	135-250	6.5-6.7	1500	3050-7450	Hinesly, Jones, and Sosewitz (1972) and Anderson (1955)
Milwaukee, Wisc.	8	-	-	435	-	130	13.5	-	1550	Anderson (1955)
Des Moines, Iowa	7	-	-	315	-	420	4.9	-	1350	Anderson (1955)
Houston, Texas	8	-	-	1035	-	65	6.?	-	950	Anderson (1955)
Rochester, N.Y.	12	-	-	1980	-	60	5.1	-	3400	Anderson (1955)
Maryland	4-12	-	-	100-490	-	60-790	2.1-118	-	610-3100	Anderson (1955)
Connecticut	160-360	-	-	465-1025	-	105-280	-	-	2200-3500	Lunt (1959)
Southern Calif.	360-680	1-140	<40-600	135-800	10-2140		2-25	15-1120	373-3400	Bradford (1973) and Dotson (1973)
Toronto, Canada	-	5-45	60-16,000	300-2400	25-170	260-450	-	185-1425	1100-9400	Van Loon and Lichwa (1973)
Oklahoma	70-100		Tr-600	800-6000	100-3000		Tr-1000		3000-7000	Thompson, Zajic, and Lichti (1964)
Indiana	-	3-810	50-19,600	300-11,700	70-3500	200-1470	-	450-1900	870-28,400	Sommers et al. (1973)

Table 6--Range of trace elements found in sewage sludge in relation to treatment process[1/]

Element	Undigested Liquid Sludge[2/]	Secondary Digestor Sludge[3/]	Vacuum Filter Cake[4/]
	----------μg/g----------		
Hg	1.2-3.4	2-56	0.6-27
Cr	66-7800	22-9600	28-10,600
Cu	200-1740	260-10,400	84-2600
Ni	44-740	14-1440	12-2800
Zn	900-8400	1120-16,400	480-9400
Cd	6-166	2-1100	2-480
Pb	150-26,000	240-12,400	80-3000
As	3-16	4-18	2.8-11

1/ From Blakeslee (1973).

2/ From 6 treatment plants.

3/ From 22 treatment plants.

4/ From 14 treatment plants.

Table 7--Extractable trace elements in 42 sewage sludges from England and Wales[1/]

Element	0.5 N HOAc Extractable		
	Range	Median	% of Total
	----------μg/g----------		
Co	0.5-77	2.5	6.2-96
Cr	<0.9-170	4.4	<0.7-8.5
Cu	2.9-1400	28	0.5-31
Mn	39-2300	190	17-91
Mo	<0.03-1.0	0.08	0.4-7.5
Ni	6.8-2400	25	15-93
Pb	4.6-150	11	0.5-10
Sn	0.06-1.6	0.5	0.1-1.6
V	0.88-7.5	2.6	1.1-14
Zn	230-11,000	1100	15-97
B[2/]	3.3-40	8.8	0.9-50

1/ From Berrow and Webber (1972).

2/ Hot water soluble.

forms of these elements vary in kind and in proportion among sludges. As far as the author is aware, no data are available on the chemical forms of trace elements which occur in sewage sludges.

Since the total concentrations of trace elements in sewage sludges reported by Berrow and Webber (1972) are somewhat comparable to concentrations in sludges from other locations, it is reasonable to expect that the ranges presented in Table 7 are representative of sludges in general.

Jenkins and Cooper (1964) present data on the amounts of Cu, Zn, and Ni extracted from sewage sludge by shaking 10 g of sludge with 250 ml of 2 percent citric acid. The air-dried sludge contained 6300 ppm Cu, 1340 ppm Ni, and 8200 ppm Zn. Two percent citric acid (pH 2.18) extracted the following amounts of trace elements (in percent of total): Cu (57.8), Ni (72.7), and Zn (75). Buffering the citric acid with ammonium citrate to higher pH's somewhat reduced the solubility of the Cu and Zn.

Water Soluble

Bradford (1973) has determined the concentrations of trace elements in aqueous saturation extracts of six sewage sludges from southern California. His data for sludges are compared to data for soils in Table 8. The values for the concentrations of trace elements in saturation extracts of soils were obtained from data reported by Bradford, Bair, and Hunsaker (1971).

Except for V, B, and Mo, the maximum concentrations of trace elements in saturation extracts from the sludges are greater than those from soils. Median concentrations of all trace elements in the saturation extracts of the sludges exceed those of saturation extracts of soils. It is noteworthy to point out that maximum concentrations of Cu, Zn, Ni, Pb, and Cd exceed the solubility products of the hydroxides and carbonates of these elements. This suggests that the chemical form of these elements which occurs in solution is in part organic since solubility product considerations would rule out inorganic forms at the concentrations observed.

Table 8--Comparison of saturation extract composition of sludges and California soils[1,2/]

Element	Range		Mean		Median	
	Sludges	Soils	Sludges	Soils	Sludges	Soils
	μg/ml					
Mo	0.10- 0.37	<0.01-22.0	0.19	0.73	0.18	<0.01
Cu	0.14- 6.0	<0.01- 0.20	1.86	0.04	1.30	0.03
Zn	0.5 - 2.5	0.01- 0.40	1.35	0.07	1.25	0.04
Ni	0.6 -18	<0.01- 0.09	3.87	0.02	1.15	<0.01
Co	0.04- 0.35	<0.01- 0.14	0.16	0.06	0.16	<0.01
Pb	0.3 - 2.0	<0.01- 0.30	0.61	0.05	0.35	<0.01
V	0.04- 0.25	<0.01- 1.20	0.09	0.07	0.05	0.01
B	2.7 -17.0	<0.10-26.0	7.95	3.06	6.80	<0.1
Cd	0.05- 2.0	<0.01	0.60	<0.01	0.12	<0.01
Ag	0.01- 0.30	<0.01	0.18	<0.01	0.20	<0.01

1/ Derived from Bradford (1973), and Bradford, Bair, and Hunsaker (1971).

2/ Data for soils represent 68 soil samples obtained from 30 soil series. Data for sludges are obtained from six metropolitan Southern California sludges.

Stones (1955, 1958, 1959a, 1959b, 1960) has evaluated trace element concentrations of sewage in relation to treatment process, and a summary of his results is presented in Table 9. Sedimentation of tank influent for a period of 12 hours (not reported in Table 9) yielded concentrations in the supernatant liquor which were lower than those of the unsettled tank influents by the following amounts (in %): Cu (45), Pb (40), Ni (21), Zn (41), and Cr (28). Sterilization of the unsettled tank influent using mercuric chloride had no effect on the trace element concentrations (Table 9). Sterilization also had no effect on the concentrations of Ni, Zn, and Cr in the supernatant liquor after 18 hours settling time. However, supernatant liquors from sterilized tank influents after 18 hours settling time had slightly greater concentrations of Cu and Pb than similarly treated unsterilized supernatant liquors. Chemical precipitation with CaO (400 ppm) followed by an 18 hour settling time produced concentrations of Cu, Pb, Ni, Zn, and Cr in the supernatant liquors which were considerably less than those of the supernatant liquors from sewage settled for 18 hours but not treated with CaO. Addition of CaO as a precipitant reduced trace element concentrations by the following amounts (in %): Cu (58), Pb (88), Ni (41), Zn (84), and Cr (35). Addition of $Al_2(SO_4)_3$ (400 ppm) to sewage as a precipitant followed by a settling time of 18 hours produced concentrations of Cu, Pb, Ni, Zn, and Cr which were 81, 91, 23, 57, and 33 percent lower, respectively, than those not treated and settled for 18 hours. Sulfuric acid as a precipitant, under similar conditions as those employed with CaO and $Al_2(SO_4)_3$, had no effect on concentrations of Cu and Ni in the supernatant liquors, but increased somewhat concentrations of Pb, Zn, and Cr in the supernatant liquors (Table 9). Biological filtration yielded concentrations of Cu, Pb, Ni, Zn, and Cr in the unfiltered effluent which were from about 20 to 40 percent lower than those of the filter feed (Table 9). One hour settlement of the filter effluent produced concentrations of Cu, Pb, Zn, and Cr in the supernatant liquor which were approximately from 35 to 60 percent less than those of the

unsettled filter effluent (Table 9). Concentrations of Cu, Pb, Zn, and Cr in the paper filtrate of unsettled filter effluent were less (65, 81, 48, and 57 percent, respectively) than those of the unsettled filter effluent (Table 9). Nickel concentrations of settled (1 hr) filter effluent and in the filtrate of paper filtered unsettled effluent were essentially the same as those of the unsettled filter effluent. This suggests that a substantial percentage of the Ni in the sewage was in the form of a soluble organic complex. In general, Stones' results indicate that high percentages of Cu, Pb, and Zn in primary sewage occur in the settleable fraction. Lesser percentages of Ni and Cr rapidly settle out from primary sewage.

Argo and Culp (1972a) recently reviewed the literature on the subject of heavy metals removal in waste water treatment. Data from their article, reproduced in Table 10 in a slightly modified and condensed form, show sand filtration is not nearly as effective in removing trace elements from sewage suspensions as is carbon adsorption and lime coagulation and recarbonation. Amounts removed from sewage by sand filtration were as follows (in %): Cd (6.6), Cr^{+6} (2.6), Cu (60), Se (9.5), Ag (11.6), Zn (76.3). Carbon adsorption removed more than 96 percent of the Cd, Cr^{+6}, and Ag, but only 37 percent of the Se. Generally, lime coagulation and recarbonation removed 90 percent or

Table 9--Trace element concentrations of sewage as influenced by treatment process[1/]

Element	Trace Element Concentration in µg/ml of:										
	Tank Influent Unsettled		Supernatant Liquor From Tank Influent After 18 hrs Settlement		Supernatant Liquor From Tank Influent After Chemical Precipitation and 18 hrs Settlement[2/]			Feed and Effluent From Biological Filters			
	Unsterilized	Sterilized[3/]	Unsterilized	Sterlized[3/]	CaO	H_2SO_4	$Al_2(SO_4)_3$	Filter Feed	Filter Effluent		
									Unsettled	After 1 hr Settlement	Paper Filtrate
Cu	0.68	0.68	0.26	0.38	0.12	0.27	0.07	0.32	0.26	0.13	0.09
Pb	0.60	0.60	0.29	0.34	0.04	0.46	0.03	0.37	0.26	0.11	0.05
Ni	0.27	0.27	0.22	0.22	0.10	0.21	0.17	0.15	0.09	0.08	0.07
Zn	1.14	1.13	0.67	0.68	0.09	0.83	0.29	0.57	0.40	0.26	0.21
Cr	0.52		0.35	0.36	0.33	0.46	0.24	0.31	0.21	0.13	0.09

1/ Derived from Stones (1955, 1958, 1959a, 1959b, 1960). Results presented are the mean of 12 or more replications.

2/ CaO, H_2SO_4, and $Al_2(SO_4)_3$ added to unsettled tank influent in amounts to yield concentrations equal to 400 ppm.

3/ Using mercuric chloride.

Table 10--Concentrations of sewage sludge effluents as influenced by treatment process[1/]

Element	Sand Filtration		Carbon Adsorption		Lime Coagulation and Recarbonation	
	Conc. Before Treatment	Conc. After Treatment	Conc. Before Treatment	Conc. After Treatment	Conc. Before Treatment	Conc. After Treatment
	mg/l					
Cd	0.00075	0.00070	0.00070	<0.00001	0.0137	0.00075
Cr^{+6}	0.0503	0.049	0.049	0.00017	0.056	0.050
Cu	0.79	0.32	-	-	15,700	0.79
					7	1.0
					7	0.05
					302	Trace
Mn	-	<0.1	-	-	2.3	<0.1
					21.0	0.05
Ni	0.08	0.1			160	0.08
					5	0.5
					5	0.5
					100	1.5
Se	0.0103	0.0093	0.0093	0.00585	0.0123	0.0103
Ag	0.00164	0.00145	0.00145	0.000048	0.0546	0.0164
Zn	0.97	0.23	-	-	-	-

1/ From Argo and Culp (1972a).

more of the trace elements studied, except again for Se and Cr^{+6} of which only 16 and 11 percent were removed. Although lime coagulation and recarbonation removed high percentage concentrations of Cu and Ni, concentrations after this treatment were generally higher than are commonly observed in soil solutions (compare data in Table 10 with those in Table 8). Data reviewed by Argo and Culp (1972a) also show that trace element concentrations of elements in sewage vary considerably. For example, Cu varies from 0.079-15,700 mg/l and Ni from 0.08-160 mg/l. Finally, this recent review article (Argo and Culp, 1972a) demonstrates the general lack of detailed and comprehensive published data on trace element compositions of sewage sludges.

In a follow-up article Argo and Culp (1972b) reported concentrations of As, Cd, Cr^{+6}, Pb, Se, Ag, Hg, Cu, and Zn in effluents from a secondary treatment plant employing trickling filters. Mean concentrations of trace elements in the effluent from the trickling filters were as follows (in mg/l): As (0.01), Ba (<0.02), Cd (0.039), Cr^{+6} (0.12), Pb (0.032), Se (0.004), Ag (0.01), Hg (0.0018), Cu (0.168) and Zn (0.50). The authors report that Cd and Cr in the trickling filter effluent exceeded the limits for injection waters established by the California Department of Public Health.

Blakeslee (1973) has reported concentrations of trace elements in filtered and unfiltered sewage effluents from 57 treatment plants in Michigan, U.S.A. His data are reproduced in condensed form in Table 11. The maximum concentrations of dissolved and total trace elements are all quite high when compared to concentrations observed in surface and well waters. Kopp and Kroner (1970), Bradford (1971), and Silvey (1967) have reported extensive data for surface and well waters and their results show maximum concentrations of trace elements which are usually less than those reported for sewage treatment effluents by Blakeslee (1973). To compare concentrations of trace elements in sewage treatment plant effluents with those commonly observed for surface waters, the data of Kopp and Kroner (1970) have been reproduced in Table 12. The median concentration of total and dissolved trace element concentrations in sewage treatment plant effluents are more or less comparable to median

Table 11--Total and dissolved concentrations of trace elements in sewage effluents from 57 Michigan, U.S.A. treatment plants[1/]

Element	Dissolved[2/]			Total[2/]		
	Range	Mean[3/]	Median	Range	Mean[3/]	Median
	----------µg/ml----------			----------µg/ml----------		
Hg	<0.02 -0.3	-	<0.2	<0.02 -1.0	0.37	<0.2
Cr	<0.01 -1.0	0.08	<0.02	<0.005-1.46	0.20	0.02
Cu	0.01 -0.55	0.07	0.03	0.01 -1.3	0.14	0.04
Ni	<0.02 -0.86	0.24	0.04	<0.02 -5.4	0.43	0.02
Zn	0.01 -1.7	0.21	0.10	0.03 -4.7	0.44	0.18
Cd	<0.005-0.04	0.016	<0.005	<0.005-0.15	0.027	<0.005
Pb	<0.02 -0.08	0.038	<0.02	<0.02 -1.3	0.14	0.02

1/ Derived from data reported by Blakeslee (1973).

2/ "Dissolved" and "Total" refer to filtered and unfiltered samples, respectively.

3/ Mean of positive values reported, i.e. removing values reported as less than the limits of detectability.

Table 12--Summary of trace element concentrations of 1577 surface waters in the United States[1/]

Element	Detection Limit[2/]	No. of Positive Occurrences	Frequency of Detection	Observed Positive Values		
				Minimum	Maximum	Mean
	mg/l		%	----------mg/l----------		
Ag	0.002	104	6.6	0.0001	0.038	0.0026
As	0.100	87	5.5	0.005	0.336	0.064
B	0.010	1546	98	0.001	5.0	0.101
Ba	0.002	1568	99.4	0.002	0.340	0.043
Cd	0.020	40	2.5	0.001	0.120	0.0095
Co	0.020	44	2.8	0.001	0.048	0.017
Cr	0.010	386	24.5	0.001	0.112	0.0097
Cu	0.010	1173	74.4	0.001	0.280	0.015
Mn	0.010	810	51.4	0.0003	3.23	0.058
Mo	0.040	516	32.7	0.002	1.5	0.068
Ni	0.020	256	16.2	0.001	0.13	0.019
Pb	0.040	305	19.3	0.002	0.140	0.023
V	0.040	54	3.4	0.002	0.300	0.040
Zn	0.020	1207	76.5	0.002	1.183	0.064

1/ From Kopp and Kroner (1970).

2/ Detection limits varied with the concentration of total dissolved solids. Those listed refer to maximum limits of detection.

concentrations observed for large numbers of surface and well water samples. The data reported in Table 11, therefore, suggest that excessive concentrations of trace elements occur in a lesser percentage of treatment plant effluents than more or less normal concentrations. Means of total concentrations of sewage treatment plant effluents are approximately 2-4 times greater than dissolved concentrations (Table 11), suggesting that effective techniques to flocculate suspended matter in effluents will reduce trace element concentrations.

Jenkins, Keight, and Ewins (1964) investigated the precipitation of Cu, Ni, Cr, and Zn by adding these metals to sewage which contained from 100-360 ppm solids. The data, however, have little value as they pertain to solubilities of these elements in sludge because the amounts added on a weight basis (μg added per unit weight of dry solids) were, in most cases, many orders of magnitude greater than would be observed in sludges. For example, the minimum concentration of Cu added in their studies would produce a concentration greater than 6000 μg Cu per gram of dry solids.

The data of Stones (1955, 1958, 1959a, 1959b, 1960), Argo and Culp (1972a, 1972b), and Blakeslee (1973) demonstrate that high percentages of the trace elements which enter sewage treatment plants are retained in the sludge fraction either precipitated or flocculated with other solids.

Trace Element Composition of Plants, Soils, and Drainage Waters From Soils as Influenced by Sewage Sludge Applications

Published accounts of studies and projects dealing with the application of sewage sludge and sewage treatment plant effluents to land as a source of irrigation water, plant nutrients, to reclaim waste water, and to improve soil physical properties are numerous. Whetstone (1965) and Law (1968) have published annotated bibliographies on the subject and each cites approximately 300 references. Very few of the references, however, deal with trace elements.

Results of studies dealing with sludge-treated land are expressed in a variety of ways. Land application rates of sludge are expressed in terms of English (short) tons of dry matter per acre, metric tons of dry matter per hectare, cubic yards per acre, surface centimeters of liquid sludge, and surface inches of liquid sludge. Dry matter weight usually refers to sludges which are air dried. The water content of the air-dried sludge is variable depending upon the kind of sewage treatment process, relative humidity, and other factors. Air dried sludges commonly range from 1-10 percent water when based upon oven dry weight (110C) (Dean and Smith, 1973) and 45-76 percent ash as determined by drying at 500C for 3-4 hours (Thompson, Zajic, and Lichti, 1964). To evaluate the results of several researchers on a comparable basis, the author has converted application rates where convenient and possible, to metric tons per hectare (1 metric ton per hectare = 0.45 English tons per acre).

Concentrations of chemical constituents in plants (roots and tops) are expressed in terms of μg element per g dry weight (70C) or fresh weight. Unless the water content is given when these are reported on a fresh weight basis it is not possible to convert to a dry weight basis; this is because water contents of fresh plant tissue are highly variable, and depend upon water stress at the time the plant is sampled, on plant species, relative humidity, and length of time harvested tissues are permitted to stand until they are weighed.

Trace elements composition of sludges and sludge-treated soils are evaluated in terms of total amount present per unit weight. This is commonly accomplished by dry ashing (500-550C for 3-4 hours) or by wet ashing with a mixture of perchloric and nitric or sulfuric acids. Empirical measures of availability to higher plants are based upon the amount extracted from soil by mineral acids (e.g., 0.1 N HCl), organic acids (acetic, citric), and chelating agents (EDTA, DTPA, etc.). The results are usually expressed on amount extracted per unit weight of soil; consequently, these values depend upon the volume of extracting solution and weight of soil used. In certain published papers, researchers have not specified the details of the methods used; where

this has occurred, I have arbitrarily assumed that the methods conform to those which I consider commonly employed.

Results are also commonly expressed in terms of part per million (ppm). The term has been rather loosely used and may be based upon fresh weight, air dry weight, oven dry weight (70-110C), weight of ash (500-600C), or on a volume basis usually assuming the density of the solution is 1.0. With respect to land applications, the term refers to pounds or kilograms per million pounds or kilograms of soil. To convert to an acre basis, the weight of soil in the surface 6 inches (15 cm) is commonly taken as equivalent to 2 million pounds, so pounds per acre is equivalent to parts per 2 million.

Trace Elements Absorbed by Plants Grown on Sludge-Amended Substrates

Trace elements applied to soils in the form of sewage sludge may be absorbed by plants. Under conditions where the plant residues are removed, the trace elements are lost from the soil system, but if plant residues are not removed, they will decay and the trace elements will be returned to the soil. The results of studies which deal with trace element absorption from sludge or compost amended soils are reviewed in some detail in the following section. No attempt has been made to review comprehensively all literature on trace element plant chemistry.

Sludge-amended nutrient solutions. One of the first reports in the United States on trace elements in sewage sludge was that of Rehling and Truog (1939, 1940). A commercial product, "Milorganite," obtained by processing sludge from a Milwaukee, Wisconsin sewage treatment plant was evaluated as a source of essential trace elements for plants. Corn, tomatoes, and sunflowers were grown in nutrient solutions which were supplied with a carbonated water extract as the only source of B, Cu, Mn, Mo, and Zn. Milorganite extracts added to the nutrient solutions after plants were grown under trace element stress resulted in resumption of normal growth and increased amounts of Cu, Mn, and Zn in the plants.

Sludge-amended soils. The work of Rohde (1962) is commonly cited as an example of one of the few studies on the long-term effects of

sewage applications upon soil trace element composition and plant growth. The research was conducted on the Berlin, Germany and Paris, France sewage farms where sewage sludges had been spread for from 50-80 years. Trace elements soluble in 10% HCl and hot water for soils beneath healthy plants were compared to those for soils beneath unhealthy plants on the Berlin and Paris sewage farms. The acid and water soluble trace elements were determined by treating 10 g of soil with 800 ml of 10% HCl or 800 ml of distilled water and refluxing one hour and 30 minutes, respectively. Results condensed from Rohde's paper are presented in Table 13. Acid-soluble Cu, Zn, Co, and Mo and hot water-soluble Cu, Zn, Co, Mo, and B were greater in soil under the unhealthy plants at the Berlin farm (Table 13). Except for Co, which is not reported, results for the Paris farm show the same trends. Acid-soluble Zn and Cu are considerably greater under the unhealthy plants and based upon these data, Rohde concludes that excessive amounts of Zn and Cu are mainly responsible for the exhaustion of sewage irrigated land. The results of Rohde (1962) are difficult to interpret since concentrations of Zn and Cu in soil beneath healthy plants are quite high when compared to normal levels observed by others (see Table 15). Also the depth to which soil samples were taken is not specified and concentrations of trace elements in sludge-treated soils are markedly dependent upon depth of sample taken. Copper and zinc are quite immobile in soils and regardless of source most of that applied remains within the depth of cultivation. Although the concentrations are not given, Rohde (1962) also reports higher amounts of Cd, Ba, Pb, and Ag in soil beneath unhealthy plants.

Le Riche (1968) presents data on the trace element concentrations of leeks, globe beets, potatoes, and carrots grown on soil treated with a total of 1260 m. tons of sewage sludge per hectare over a period of 19 years or an average annual rate of 66 m. tons/hectare. The experiments showed no adverse effects on crop yields, but the plants accumulated abnormally large amounts of certain trace elements. Yield results along with major nutrient status were reported by others (Mann and Patterson,1962; Garner, 1966). Globe beet and potatoes grown

Table 13--Ten percent HCl and hot water soluble trace elements in soil under healthy and unhealthy plants[1/]

Element	Berlin Sewage Farm		Paris Sewage Farm	
	Healthy Plants	Unhealthy Plants	Healthy Plants	Unhealthy Plants
	10% HCl Soluble (μg/g)			
Mn	116	97	216	166
Cu	118	508	132	291
Zn	197	609	386	1032
Co	1.8	3.0	-	-
Mo	1.7	2.6	2.3	3.1
B	2.1	2.0	3.3	5.3
	Hot Water Soluble (μg/g)			
Mn	6.9	4.3	3.1	2.4
Cu	8.7	20.1	8.5	11.2
Zn	6.5	19.1	3.4	10.5
Co	0.16	0.30	2.3	3.6
Mo	0.25	0.59	1.4	1.5
B	1.3	1.8	0.40	0.46

1/ From Rohde (1962). Concentrations are expressed in terms of amount of element solubilized per unit weight of soil.

on the sludge-treated land contained significantly larger concentrations of Ni and Zn but not of Cu, Pb, Mo, and Cr. The Ni and Zn were more concentrated in the tops than in the roots, and there was no evidence that any of the elements accumulated in potato tubers. Leek plants from plots receiving the sludge contained significantly higher concentrations of Cu, Ni, and Zn. Carrots grown on the sludge plots 6 years after treatments were discontinued showed higher concentrations of Cr, Mo, Ni, and Zn in the tops than carrots grown on untreated plots. The plant results are summarized in Table 14. The concentrations of Cu, Cr, and Mo are in the range reported as intermediate for a wide variety of crops, but concentrations of Ni and Zn are generally higher than normally found in plant tops (Chapman, 1966; Allaway, 1968; Jones, 1972). For reference, concentration of trace elements typically found in plants and soils, as reported by Allaway (1968), are presented in Table 15.

The amount of Cr, Cu, Ni, Pb, and Zn dissolved in 0.5 N HOAc for the sludge, sludge-treated soils 7 years after the treatments were discontinued, and untreated soils are also reported by Le Riche (1968). These results presented in Table 16 show some accumulation of trace elements in the treated soil. Levels of trace elements normally extracted from surface layers of arable Scottish soils by 2.5% HOAc (0.5 N) and 0.05 N ethylenediaminetetraacetic acid (EDTA) as reported by Mitchell (1964) are reproduced in Table 17. Acetic acid-soluble Cr and Pb in the sludge-treated soils used in Le Riche's studies are in the range considered normal by Mitchell (1964), but concentrations of Cu, Ni, and particularly Zn, are somewhat greater than normal. The 0.5 N HOAc soluble zinc for the sludge-treated soil, 275 µg/g, is in excess of the level of 200 µg/g considered by Purves (1972) to be indicative of Zn toxicity to a number of crops.

Lunt (1959) studied the influence of applications of six sewage sludges from Connecticut, U.S.A., on seed germination, plant growth and composition, and soil properties. Two sludges added to pots at a rate of 22 m. tons dry matter per hectare (10 tons/acre) caused 20 to 67 percent reduction in germination of lettuce and radish seeds. Additional studies using aqueous extracts of the sludges on heavy

Table 14--Trace element composition of crops grown on soil treated with sludge at an average rate of 66 m. tons/ha/year for 19 years[1/]

Treatment	Concentrations of Trace Element in Plants				
	Cr	Cu	Mo	Ni	Zn
	μg/g dry matter				
			Leeks		
Untreated	0.71	5.7	0.50	2.0	46
Treated	0.54	16.0	1.10	7.0	135
			Globe Beet Tops		
Untreated	0.85	8.5	0.45	3.2	169
Treated	1.0	10.0	0.65	16.5	>505
			Globe Beet Roots		
Untreated	0.3	11	0.1	1.65	102
Treated	0.8	18	0.25	13.0	250
			Potato Tops		
Untreated	1.70	4.2	0.37	1.7	90
Treated	3.0	8.2	1.0	5.2	120
			Potato Roots		
Untreated	0.09	9.5	0.40	0.25	30
Treated	0.03	9.5	0.27	0.57	27
			Carrot Tops		
Untreated	0.41	8.2	0.58	1.28	47
Treated	0.88	9.9	0.84	3.0	99
			Carrot Roots		
Untreated	0.03	6.3	0.12	-	34
Treated	0.06	4.6	0.12	-	42

1/ From Le Riche (1968). Leeks, beets, and potatoes are means of 2 plots. Carrots were grown on soil 7 years after treatments were discontinued.

Table 15--Total concentrations of trace elements typically found in soils and plants[1/]

Element	Conc. in Soils (µg/g)		Conc. in Plants (µg/g)	
	Common	Range	Normal	Toxic[2/]
As	6	0.1 -40	0.1 -5	-
B	10	2 -100	30 -75	>75
Cd	0.06	0.01-7	0.2 -0.8	-
Cr	100	5 -3000	0.2 -1.0	-
Co	8	1 -40	0.05-0.5	-
Cu	20	2 -100	4 -15	>20
Pb	10	2 -200	0.1 -10	-
Mn	850	100 -4000	15 -100	-
Mo	2	0.2 -5	1 -100	-
Ni	40	10 -1000	1	>50
Se	0.5	0.1 -2.0	0.02-2.0	50-100
V	100	20 -500	0.1 -10	>10
Zn	50	10 -300	15 -200	>200

1/ From Allaway (1968).

2/ Toxicities listed do not apply to certain accumulator plant species.

Table 16--Trace elements extracted from soil and sludge by 0.5 N HOAc[1/]

Material	Trace Element				
	Cr	Cu	Ni	Pb	Zn
	----------μg/g dry matter----------				
Sludge[2/]	3.5	20	50	3.2	800
Sludge Treated Soil[3/]	2.6	57	8.1	4.2	275
Untreated Soil	0.9	15	3.4	1.6	83

1/ From Le Riche (1968).

2/ Mean of sludge sampled in 1958 and 1959.

3/ Treated at a rate of 66 m tons per hectare per year for 19 years.

Table 17--Trace elements normally extracted from surface layers of arable Scottish soils[1/]

Element	Amount Extracted by: 0.5 N HOAc	0.05 M EDTA
	μg/g	
Co	0.05-2.0	<0.05-4.0
Cr	<0.01-1.0	0.1 -4.0
Cu	<0.05-1.0	0.3 -10
Mn	5-100	5-100
Mo	<0.02	<0.03-1.0
Ni	0.1 -5.0	0.2 -5.0
Pb	<0.2 -4.0	1.0 -10.0
Sn	<0.5	<0.5
V	<0.05-1.0	0.2 -5.0
Zn	<2-30	<3-20

1/ From Mitchell (1964).

blotting paper showed that the principal effect of the sludge was to delay rather than inhibit germination. In general, as the application rate increased, the time delay in germination also increased. Hinesly, Braids, and Molina (1971) also present data which show that sewage sludge may inhibit seed germination.

The trace element composition of oats, spinach, turnips, and beets in relation to amounts of sludge applied to soils in pots in the greenhouse as reported by Lunt (1959) are reproduced in Tables 18 and 19. Levels of Cu, Mn, and Zn reported for plants grown on sludge treated and control soils are higher than those normally observed for many crops (Allaway, 1968; Jones, 1972). Boron in the plants does not appear to be related to sludge application rates (Tables 18 and 19). Concentrations of Cu appear to be related to plant species and soil reaction. With oats, spinach, and turnip greens on the acid and neutral soils, sludge treatment had no consistent effect on Cu concentration in the plants (Tables 18 and 19). However, in the case of beets, concentrations of Cu in tops increased in relation to treatment in both the acid and neutral soil. Zinc in the tops of all plants tested increased as the amount of sludge applied to the soil increased, regardless of the soil pH (Tables 18 and 19). Generally, the increase in Zn in relation to sludge treatment was more profound in the acid soils. The results show plant species effects and that concentrations of Zn and Cu in plant tops can be reduced by increasing soil pH. Similar observations have been made by others (Chaney, 1973; Terman, Soileau, and Allen, 1973).

Patterson (1971) has reviewed the results of a number of studies on effects of sewage sludge applications to agricultural land conducted by the National Agricultural Advisory Service regional soil science laboratories in England (the results of these studies were reported in internal reports and as such are not available for general distribution). According to Patterson (1971), instances of crop damage caused by accumulations of toxic levels of one or more trace elements in soils which had repeatedly received annual applications of sewage sludge are sufficiently common in England so they are known to every agricultural advisor. Severe damage to vegetable crops was reported on a soil which

Table 18--Trace element composition of oats and spinach grown in pots treated with various levels of sewage sludge[1/]

Treatment	Rate[2/] (m. tons/ha)	Element (µg/g)[3/] B	Cu	Mn	Zn
		Oat Tops - Acid Soil			
Check	-	39	65	240	240
Torrington	44	35	54	280	575
Sludge	88	35	57	250	835
	176	30	54	400	1185
West Haven	22	30	41	355	245
Sludge	44	31	43	475	255
	88	29	40	665	385
		Spinach Tops - Neutral Soil			
Check	-	40	23	190	525
Torrington	44	42	53	160	660
Sludge	88	42	49	140	765
	176	39	65	150	815
West Haven	22	47	34	365	755
Sludge	44	41	35	825	830
	88	41	46	2280	1200

1/ From Lunt (1959).

2/ Approximate - Rate presented by author has been converted from cu yds/acre to m. tons/ha.

3/ Although not stated by author, it is assumed results are expressed on dry wt. basis.

Table 19--Trace element composition of turnips and beets grown in pots treated with various levels of sewage sludge[1/]

Treatment	Rate[2/] (m. tons/ha)	Element (µg/g)[3/] B	Cu	Mn	Zn
		Turnip Greens - Acid Soil			
Check	-	53	62	70	-
Torrington	44	53	90	80	385
Sludge	88	53	70	120	500
	176	50	80+	120	800
West Haven	22	51	46	80	185
Sludge	44	51	45	150	340
	88	48	60	190	355
		Beet Tops - Neutral Soil			
Check	-	59	51	90	-
Torrington	44	36	54	75	85
Sludge	88	42	80+	100	195
	176	42	95+	95	230
West Haven	22	58	39	135	-
Sludge	44	54	69	130	-
	88	35	100+	100	160

1/ From Lunt (1959).

2/ Approximate - Rate presented by author has been converted from cu yds/acre to m. tons/ha.

3/ Although not stated by author, it is assumed results are expressed on dry wt. basis.

had received 45 m. tons of sludge per hectare per year for 30 years. The surface soil from the treated area had the following trace element concentrations (in ppm): Zn (5000), Cu (500), Pb (1500), Cr (150), and Ni (50). No results were reported for the trace element composition of the sludge applied. Toxicities to sugar beets were recorded on sludge-treated soils which showed the following amounts of trace elements extracted from the soil by 0.5 N HOAc (in μg/g): Zn (420), Ni (2.0), Cu (0.24). Twenty-four instances of damage to crops from sewage sludge applications to soil were observed where 0.5 N HOAc extractable Zn varied from 66-1500 μg/g; crop damage, however, was not necessarily attributed to a Zn toxicity. Poor growth of oats and potatoes grown on some sewage-treated lands was attributed by Patterson (1971) to Ni toxicity. In the area of poor growth, concentrations of Ni extracted with 0.5 N HOAc were 20-34 μg Ni/g. Oats grown in acid soil (pH 5.3) treated with a sewage sludge high in Ni at rates of 0, 34, 67, and 134 m. tons sludge per hectare showed yield reductions at the 134 m. ton/hectare rate; but in the same soil adjusted to pH 6.8, yield was unaffected. The sludge applied contained 920 ppm Cu, 2400 ppm Cr, 8700 ppm Zn, and 6480 ppm Ni, all expressed as total concentrations on a dry weight basis. Nickel and Cu analyses of the oat plants reported by Patterson (1971) are reproduced in condensed and slightly modified form in Table 20. The rate of sludge application had no significant effect on the amounts of Cu absorbed by the plants at both soil pH's. However, Ni was absorbed by the plants in substantial amounts when sludge was applied to both the acid and neutral soil, with amounts absorbed by plants grown in the acid soil considerably greater than those absorbed by plants grown in the neutral soil (Table 20). At application rates greater than 67 m. tons/ha the Ni concentrations of the oat plants were greater than levels considered toxic by Allaway (1968). Additional studies reported by Patterson (1971) show rather dramatically the influence of pH on Ni toxicity to and absorption by plants. Wheat was grown on a soil adjusted to various pH values (5.1-7.5) to which were added increasing amounts of Ni (as $NiSO_4$). Application rates ranged from 5-160 μg Ni/g soil. In the soil at pH 5.1 six weeks

Table 20--Copper and nickel concentrations in oat plants as influenced by amount of sewage sludge applied and soil pH[1/]

Amt. Sludge Applied (m. tons/ha)	Conc. in Soil (μg/g)[2/]		Conc. in Plants (μg/g)[3/]			
			Cu		Ni	
	Cu	Ni	pH 5.3	pH 6.8	pH 5.3	pH 6.8
0	-	-	11	13	8	4
33	14	97	12	12	90	28
67	28	194	12	12	120	50
134	56	389	19	14	210	70

1/ Condensed and modified from Patterson (1971).

2/ Disregarding amount present initially; concentrations in soil are based upon air dry weight.

3/ Concentrations in plants are on a dry matter basis.

after sowing, Ni toxicity symptoms and yield depressions were severe, moderate, and slight on plants grown in soils treated with 80, 40, and 20 μg Ni/g, respectively. At pH 7.5 Ni treatment had no visible effect on the plants. Concentrations of Ni in the wheat plants in relation to treatment and soil pH reported by Patterson (1971) are reproduced in Table 21. Uptake of Ni in soils at pH 6.5 and 7.5 for Ni application rates up to and including 80 μg/g were slight and not substantially different from the controls (no Ni added to soil), but plants grown in the Ni treated soils at pH 5.1 and 5.5 absorbed rather large amounts of Ni (Table 21). According to Patterson (1971), levels of total Ni greater than 20 μg/g in soils of pH 5.5 or less may damage several crops. Toxic levels for neutral, alkaline, and calcareous soils are much higher. Hunter and Vergnano (1952) report that plants differ markedly relative to their susceptibilities to Ni toxicity.

Studies at Wye, England, showed that a single application of sludge to a soil at pH 7.7 at rates up to 365 m. tons/ha produced no visible damage to radishes (Patterson, 1971). The sludge contained 200-504 ppm Cu, but the Cu concentration in the tops and roots of the radishes was unaffected by application rates up to 365 m. tons/ha.

Hinesly, Jones, and Ziegler (1972) have studied the effects of applications of heated anaerobically-digested sewage sludge from the Metropolitan Sanitation District of Greater Chicago (MSDGC) on growth and chemical composition of corn. The sludge was applied during the growing season as a slurry containing about 3.4 percent solids at rates of 1/4, 1/2, and 1 inch as frequently as drying conditions of the sludge would permit. The sludge applications increased yield of corn grain each year for a four-year period (1968-1971) but yield increases were significant in only one of the four years. Amounts of trace elements applied per year in sludge for the maximum rate used averaged the following (in kg/ha): Zn (510), Cu (132), Mn (44), Mo (0.12), B (4.4), Cr (316), Co (0.30), Se (0.38), Ni (32), Pb (112), Hg (0.038), Cd (35.8), and Sn (4.5). Sludge treatments had no significant effect on concentrations of Cr, Cu, Pb, Ni, and Hg in corn leaves sampled at tasseling stage during the third year of the study. Similarly, treatments had no significant

Table 21--Effect of Ni applied to soils at different pH levels on the Ni content of spring wheat[1/]

Ni Applied	Conc. of Ni in Plants Grown in Soil at pH: 5.1	5.5	6.5	7.5
µg/g soil	----------µg Ni/g dry matter----------			
0	2.5	2.2	1.0	-
5	4.5	2.5	0.75	0.5
10	3.0	3.7	2.2	0.5
20	8.0	4.7	2.0	-
40	10.0	6.5	2.75	0.75
80	74.0	17.2	3.0	1.25
160	-	105.	8.25	3.0

1/ From Patterson (1971).

effect on concentrations of Mn, Cr, Cu, Pb, Ni, B, and Hg in corn grain sampled during the third year. Concentrations of Mn, Zn, Cd, and B in corn leaves and corn grain from plants grown on soils receiving the sludge treatments and sampled after the third year of the study reported by Hinesly, Jones, and Ziegler (1972) are presented in Table 22. The data show that for the maximum treatments concentrations of Mn, Zn, Cd, and B in the leaves increased by factors of about 1.4, 3.7, 3.5, and 1.7, respectively. The authors state that corn plants did not accumulate toxic concentrations of trace elements. However, accumulations observed apply to a 3-year duration, and if rates of application were to continue annually at the same levels, since the plants do absorb certain potentially toxic trace elements, the data suggest that the soils may build up toxic concentrations of trace elements, particularly Zn and Cd, in the future years. Evidence that this may occur is provided by studies conducted in England (Patterson, 1971) and Germany and France (Rohde, 1962).

Andersson and Nilsson (1972) in Sweden have evaluated the influence of sewage sludge applications to soil on trace element enrichment of soils and plants. The sewage sludge was applied at an average annual rate of 7 m. ton dry matter per hectare per year every other year commencing in 1956. At the time fodder rape plant samples were taken, a total of 105 m. tons/ha (~47 s. tons/acre) sewage sludge had been applied. Sludge application rates in this study are somewhat less than those which have been commonly used in the U.S.A. and England; for example, the maximum sludge treatment used in the studies of Hinesly, Jones, and Ziegler (1972) corresponded to a total of 270 m. tons/ha (118 s. tons/acre) over a 4-year period or approximately 2.6 times the total amount applied in the Swedish study over a 15-year period.

Concentrations of trace elements in fodder rape plants in relation to concentration in the sludge applied, and total amount of each element applied from sludge as reported by Andersson and Nilsson (1972) are presented in slightly modified form in Table 23. Although plants grown on sludge-treated soils showed higher concentrations of trace elements, except for Cd and Se, they were not particularly high compared to plants in

Table 22--Total contents of trace elements in corn as influenced by amounts applied from a sewage sludge source[1/]

Element	Amt. Trace Element Applied From Sludge[2/]	Amt. Found in Leaves	Amt. Found in Grain
	kg/ha	------μg/g dry weight-------	
Mn	0	81	18
	33	83	14
	66	92	11
	132	116	18
Zn	0	58	89
	380	85	93
	760	138	127
	1520	212	152
Cd	0	3.3	0.3
	27	3.0	0.6
	54	5.3	0.8
	108	11.6	1.0
B	0	26	7.1
	3.3	32	6.2
	6.6	35	5.4
	13.2	44	6.6

1/ Condensed and modified from Hinesly, Jones, and Ziegler (1972).

2/ Approximate, extrapolated from data presented.

Table 23--Trace element concentrations of fodder rape as influenced by repeated applications of sewage sludge[1/]

Element	Conc. in Sludge	Total Amt. Applied in Sludge	Conc. in Vegetation	
			Control	Sludge Treated
	µg/g	kg/ha	µg/g	
Mn	373	39.1	36	41
Zn	4890	513	34	114
Cu	1960	206	3.9	8.3
Ni	88	9.2	4.9	9.2
Co	122	1.3	1.6	1.9
Cr	176	18.5	2.6	4.1
Pb	293	30.8	5.2	7.7
Cd	11	1.2	0.6	0.6
Hg	12	1.3	0.033	0.049
Mo	7.4	.78	1.1	1.7
As	6.6	.69	0.37	0.73
B	30	3.2	29	36
Se	7.3	.77	0.07	0.06

1/ Condensed and modified from Andersson and Nilsson (1972). Concentrations are expressed on a dry matter basis.

general. Levels of all elements in the plants are in the range reported as intermediate for many plants (Chapman, 1966), and normal by Jones (1972) and Allaway (1968). Zinc and mercury were accumulated to the greatest extent, but their concentrations are still well below levels considered toxic (Chapman, 1966). The trace element composition of the sludge is not excessive when compared to sludges from many metropolitan areas (see Table 5).

King and Morris (1972a, 1972b) have studied the effect of applications of liquid sewage sludge (mean of 6.3 percent solids) to a sandy clay loam soil on growth and chemical composition of coastal bermuda grass and rye. Over a two-year period, the amounts of sludge applied varied from approximately 42-242 m. tons/ha (oven dry wt., 110C basis). Dry matter yield of coastal bermuda grass harvested during the second year of the study for treatments greater than about 40 m. tons/ha/year were significantly greater than the controls (no sludge or inorganic fertilizer added) but were not significantly different from treatments where only inorganic fertilizers (NPK) were added. The effect of the sludge treatments on the Mn, B, Cu, Mo, and Ni concentrations of the bermuda grass were slight or insignificant, but the concentration of Zn in the highest treatment reached levels which were 16 times the levels in the control and inorganic fertilizer treatments. These high levels of Zn had no effect on yield or "in vivo" digestibility of the bermuda grass.

In a follow-up study to investigate residual effects of sludge applications to soil, King and Morris (1972b) seeded their experimental plots to rye. Cumulative amounts of trace elements applied in sludge over the course of the two years were as follows (in kg/ha): Mn (46), B (5), Cu (116), Zn (612), Mo (3.2), and Ni (6.4). Yields of rye for the first year's harvest on plots treated with sludge were significantly greater than those for the controls, and except for the lowest sludge treatment (42 m. tons/ha), they were not significantly different from those on plots treated with inorganic fertilizers (NPK). Lower yield for the low sludge treatment was probably due to a N deficiency. The fertilized (NPK) plots were split at the end of the first year, and one-half of each

plot was limed at a rate equivalent to 6.7 m. tons/ha. Lime was added because the pH of the soil to a depth of 30 cm for the 121 and 242 m. tons/ha treatments had dropped from about pH 5.2 to levels, depending upon depth, of pH 4.2 to pH 4.9. Rye yields for the 2nd planting for plots treated at the maximum sludge rate on unlimed and limed plots were about 20 and 50 percent, respectively, of yields of plots which received only NPK fertilizer (Table 24). The differences were highly significant.

Trace element composition of rye clippings sampled from the second year of the study as reported by King and Morris (1972b) are presented in a condensed and slightly modified form in Table 24. Concentrations of Mo in the plants were 4.0-4.8 ppm and not influenced by sludge treatment. In the sludge-treated soils, lime applications reduced concentrations of Mn, Cu, and Zn in the rye plants. Concentrations of Zn and Cu in both limed and unlimed plots which received maximum sludge applications are in the range reported to reduce yields of many crops and the authors suggest that reduced yields are associated with the high levels of Cu and Zn. Zinc extractable with $\underline{N}$ NH_4OAc (pH 7) from the maximum sludge-treated soil at a depth of approximately 5 cm was about 4 times greater than that in the controls (5 compared to 20 kg Zn/ha).

Amounts of trace elements removed from the sludge-treated plots by bermuda grass and rye are also reported by King and Morris (1972b). Amounts recovered in the crops for the maximum sludge treatment were as follows (in percentage of that applied): Mn (14), B (4), Cu (0.3), Zn (1.0) and Mo (2.0).

Jones, Hinesly, and Ziegler (1973) recently reported the Cd concentration of soybean plants grown on sewage-sludge amended soils. Digested sludge containing 129 μg Cd/g was added to soils at rates up to 87 m. tons/ha. Soybean plants grown on the treated soils in pots in the greenhouse absorbed significant amounts of Cd. The concentration of Cd in the tops of soybean plants grown for 95 days in soil treated at the maximum rate (87 m. tons/ha) was 18.5 μg/g dry matter compared to 1.8 μg/g for the controls (no sludge added). Soybean seeds from plants

Table 24--Trace element composition and yield of rye clippings as influenced by sludge applications to soils[1/]

Sludge Rate[2/]	Treatment	Yield[3/]	Trace Element Conc.[3/]			
			Mn	B	Cu	Zn
m. tons/ha		kg/ha	----------µg/g----------			
0	unlimed	2,000	128	5.0	10.0	32
	limed	2,120	93	6.2	10.2	30
42	unlimed	1,180	84	5.0	11.0	150
	limed	1,570	72	6.2	10.2	106
84	unlimed	1,540	133	8.8	12.5	232
	limed	1,960	89	6.8	11.5	186
121	unlimed	1,650	111	6.5	14.5	340
	limed	2,090	82	7.5	12.0	251
242	unlimed	390	227	8.8	20.0	775
	limed	900	161	6.5	16.0	579

1/ Condensed from King and Morris (1972b). All treatments were treated with NPK inorganic fertilizer at recommended rates.
2/ Total applied on an oven dry weight (110C) basis over a two year period.
3/ Dry weight basis.

grown on soils treated at the maximum sludge rate showed Cd concentrations of approximately 1.0 μg/g.

Linnman, et al. (1973) report Cd concentrations for wheat grown on soils adjusted to various pH with CaO and treated with sewage sludge. The sludge contained 10 μg Cd/g dry matter and was applied to the soils at rates up to 175 m. ton/ha. At the maximum rate the Cd added to the soil was relatively low, 0.84 μg/g soil. Cadmium uptake by wheat generally increased with sludge application rate but was also influenced by the pH of the soil. Maximum uptake, 0.26 μg Cd/g dry matter, occurred at pH 5.3 with an application rate of 58 m. tons/ha. Minimum uptake, 0.03 μg Cd/g dry matter, occurred at pH 7.4 in the control soil.

Compost amended soils. Recently a few studies have been conducted on the effects of applications of municipal waste composts to soils on plant performance and chemical composition (Terman and Mays, 1973; Terman, Soileau, and Allen, 1973; Mays, Terman, and Duggan, 1973). The composts are prepared by combining dry garbage refuse solids with up to 20 percent sewage sludge. Details of the composting operation cited above are described by Kochtitzky, Seaman, and Wiley (1969). Additionally, Hart (1968) has reviewed composting operations in Europe.

Hortenstine and Rothwell (1972) incorporated municipal refuse (compost) into the top 15 cm of phosphate-mining sand tailings at rates of 35 and 70 m. tons/ha with and without nitrogen, phosphorus, and potassium (NPK) fertilizer for a two-year period. Sorghum and oats were grown on the amended soils. The composts contained approximately 40 μg B/g and 639 μg Zn/g. Sorghum and oat plants grown on the compost-amended soils at the 70 m. ton/ha rate contained significantly higher concentrations of both B and Zn, demonstrating at least partial plant availability of these elements from the municipal compost.

Terman, Soileau, and Allen (1973) applied a compost prepared by combining sewage sludge with municipal refuse (up to 20% sewage sludge) to an acid soil (pH 4.1) at rates of 0, 45, and 90 m. tons/ha. Fescue forage was grown in the greenhouse for a period of 10 months on the treated soils with and without lime and NPK fertilizer. The compost applied contained 1500 μg Zn/g. Yields of fescue were increased by compost applications where no additional

fertilizer was applied, but where NPK fertilizers were applied additional increases in yield were observed (Table 25). Liming depressed the uptake of Zn for all treatments (Table 25). Although Zn levels were higher in the fescue grown on unlimed soils, they were below levels considered toxic to fescue.

In another study Terman, Soileau, and Allen (1973) grew corn and snap beans on an acid soil (pH 4.9) which was limed and compost treated. Again liming reduced Zn uptake. Corn and snap beans grown on the compost-treated soil contained more Zn than the control soil at approximately the same pH, and when the compost-treated soil was acidulated, zinc absorption by corn and snap beans more than doubled. Mays, Terman, and Duggan (1973) also have shown that compost applications increase concentration of Zn in forage sorghum grown in the field.

A certain amount of data have been published on trace element compositions of plants and soils adjacent to mining operations. In the present study no attempt has been made to review the literature on soil and vegetation contamination resulting from mining operations. Recent reviews on this subject have been published by Antonovics, Bradshaw, and Turner (1971), and Little and Martin (1972).

Trace Element Composition of Soils Following Applications of Sewage Sludge

Published information on trace element composition of sludge-amended soils is meager. A few reports cover either the total trace element composition, or concentrations of trace elements extracted from soil with various reagents such as mineral acids, organic acids, buffered salts, and chelating agents. Essentially no information is available on the chemical form or ion species of the various trace elements which occur in sludge-amended soils. Reports which deal with trace element composition of soils as they relate to plant growth and trace element concentrations have been covered under the section entitled "Trace Elements Absorbed by Plants Grown on Sludge-Amended Substrates."

Table 25--Yields and concentrations of zinc for fescue forage in relation to compost and lime applications[1/]

Soil Treatment		No NPK		NPK	
Compost	Lime	Dry Matter Yield	Zn Conc.	Dry Matter Yield	Zn Conc.
---m. tons/ha----		g/pot	µg/g	g/pot	µg/g
0	0	0	-	0.2	-
0	6.7	0.5	-	24.4	78
0	13.4	0.8	-	28.5	60
45	0	3.4	141	25.6	163
45	6.7	5.1	79	29.4	92
45	13.4	5.0	64	28.6	74
90	0	8.6	110	33.4	122
90	6.7	10.3	86	33.1	102
90	13.4	10.6	75	34.7	85

1/ Condensed and modified from Terman, Soileau, and Allen (1973).

Purves (1972) has examined the trace element composition of a number of sludge-amended soils and soils from urban and rural areas in Great Britain. Results of these studies show elevated concentrations of B, Cu, Pb, and Zn in sludge-amended and urban soils. However, concentrations of these elements in the soil were below those considered damaging to plants. Purves points out that contamination of soil with respect to Cu, Zn, and Pb is virtually permanent, and he expresses concern over potential trace element hazards associated with prolonged annual applications of sewage sludge.

Peterson and Gschwind (1973) applied sewage sludge to acid mine spoil material in columns at rates equivalent to 61 and 122 m. tons/ha and leached the columns with aerated de-ionized water for a period of 110 days. The sludge used was from the Metropolitan Sanitation District of Greater Chicago (MSDGC) and contained relatively high concentrations of Cd, Cr, Cu, Ni, and Pb. As indicated by concentrations soluble in 0.1 N HCl following leaching, rather large amounts of Zn, Cu, and Cr were retained in the spoil columns (Table 26). Sludge applications at rates of 61 m. tons/ha and 122 m. tons/ha increased the leachate pH from about pH 2.4 to pH 5.0 and 6.2, respectively. The amounts of Zn, Cr, and Cu extracted from the sludge-treated acid mine spoil material with 0.1 N HCl are quite high compared to those of the controls and soils in general. Concentrations of Zn extracted from agricultural soils with 0.1 N HCl usually do not exceed 20 µg/g. It is also worthy to note that Peterson and Gschwind's data (Table 26) show that concentrations of trace elements in the columns vary with depth. Concentrations in the profile also vary with rate of application.

Hinesly, Jones, and Ziegler (1972) evaluated the total and 0.1 N HCl extractable trace element concentration of soils treated with surface applications of MSDGC sludges at rates equivalent to approximately 44, 88, and 166 m. tons/ha. In the surface 15 cm of soil, the amounts of Cr, Cu, Pb, Ni, Zn, and Cd extracted with 0.1 N HCl from the sludge-amended soils are considerably greater than those in the controls (Table 27). Concentrations of the extractable trace elements were considerably lower in the 30-45 cm depth increment, indicating that Cr, Cu, Pb, Ni, and Zn are quite immobile in soil.

Hinesly, Jones, and Ziegler (1972) also report the total concentration of trace elements in the surface 15 cm of soil following

Table 26--Concentrations of various trace elements extracted from sludge-amended acid spoil mine material[1/]

Treatment[2/]	Spoil Depth	0.1 N HCl Extractable			
		Mn	Zn	Cu	Cr
m. tons/ha	cm	----------µg/g----------			
Control		8.0	54	14	4.3
61	0 - 10	7.7	136	33	20
	10 - 20	3.5	145	5.5	3.5
	20 - 30	21	556	126	77
	30 - 40	19	488	127	78
122	0 - 10	12	404	80	52
	10 - 20	10	206	67	51
	20 - 30	5.5	113	7.1	5.2
	30 - 40	3.8	70	6.4	3.8

1/ From Peterson and Gschwind (1973).

2/ Sewage sludge was incorporated uniformly to 2 kgm of spoil material at rates indicated.

Table 27--Concentrations of trace elements extracted with 0.1 N HCl from sludge-amended soils[1/]

Application rate	Conc. in Soil (μg/g)						
	Mn	Cr	Cu	Pb	Ni	Zn	Cd
m. tons/ha							
			0 - 15 cm depth				
0	304	0.94	3.9	6.6	2.3	13	0.2
44	306	3.3	8.4	11	3.5	41	1.5
88	428	11	19	17	5.3	98	3.8
166	402	19	32	30	7.0	181	7.0
			30 - 45 cm depth				
0	45	0.6	3.5	2.0	2.6	7.8	0.6
44	63	0.8	4.9	2.7	3.6	12	0.7
88	57	1.3	5.9	4.2	3.6	16	0.8
166	61	1.6	6.4	5.3	3.6	18	0.9

1/ From Hinesly, Jones, and Ziegler (1972).

treatment with up to 166 m. tons per hectare of sludge over a three-year period (Table 28). From these data and others provided for the amounts of trace elements applied from sludge, it is possible to estimate the percentage of trace elements applied which are recovered in the surface 15 cm of soil. Percentage recoveries in the surface 15 cm, as computed from the data of Hinesly, Jones, and Ziegler (1972), are presented in Table 28. The data indicate that from 33-56 percent of the Pb, Ni, and Zn applied are retained in the surface 15 cm of soil, that Cu retention is slightly lower (27-31%), and that Cr and Cd are retained to the extent of 17-26 percent. Trace metals not retained in the surface 15 cm are removed by plants, transported to depths below 15 cm, or eroded from the surface.

Le Riche (1968) examined the concentrations of trace elements extracted by 0.5 N HOAc from soils which were treated with a total of 1260 m. tons of sludge/ha over a period of 19 years. His results, reproduced in Table 29, show substantial increases of Cr, Cu, Ni, Pb, and Zn in the sludge-amended soils. Amounts of Zn extracted by 0.5 N HOAc from the sludge-amended soils (210-430 µg/g) exceed the level of 150 µg/g considered by Patterson (1971) to cause yield reductions of many susceptible crops. Also, Ni and Cu extracted from the soil with 0.5 N HOAc are in the general range considered to be damaging, particularly to sensitive crops.

The sludge treatments were discontinued after 1961; amounts of trace elements extracted by 0.5 N HOAc six years after the treatments were discontinued are also shown in Table 29. The results show that time (6 yrs.) resulted in some reduction in extractable Ni, Pb, and Zn. This reduction is possibly due to leaching, plant absorption, and reversion of these elements to a form less soluble in 0.5 N HOAc. Extractable Cr remained about the same, and extractable Cu increased. The change in extractable Cu may be due to sampling and analytical errors. These results indicate that trace elements applied to soils in the form of sewage sludge persist in a form considered at least moderately available to plants for long periods of time.

Table 28--Recovery of trace elements in the surface 15 cm of sludge-amended soils[1/]

Element	Amt. Sludge Applied	Amt. Trace Element Applied	Content in 0-15 cm Depth	Recovery in 0-15 cm Depth
	m. tons/ha	----------kg/ha----------		%
Cr	0	0	55	-
	88	406	118	26
	166	811	164	19
Cu	0	0	36	-
	88	170	64	31
	166	339	100	27
Cd	0	0	2.1	-
	88	46	9.7	20
	166	92	16	17
Pb	0	0	59	-
	88	144	84	41
	166	289	114	33
Ni	0	0	44	-
	88	41	48	56
	166	82	53	42
Zn	0	0	137	-
	88	652	310	39
	166	1305	596	41

1/ Estimated from data of Hinesly, Jones, and Ziegler (1972).

Table 29--Trace elements extracted by 0.5 N HOAc from soils treated with sewage sludge for 19 years and the sewage sludge applied[1/]

Description	Concentration Extracted by 0.5 N HOAc:[2/]				
	Cr	Cu	Ni	Pb	Zn
	μg/g				
Sewage Sludge Applied	3.5	20	50	3.2	800
Control:					
Sampled in 1959	0.3	5	4.2	1.2	88
Sampled in 1967	0.9	15	4.4	1.6	83
Treated[1/]:					
Sampled in 1959	2.8	20	18	5	395
Sampled in 1967	2.6	58	8.1	4.2	275

1/ From Le Riche (1968). Sewage sludge was applied annually at an average rate of 66.5 m. tons per hectare per year for 19 years.

2/ Results are the mean from 2 plots.

3/ Treatments were discontinued after 1961. In 1959 and 1967 the total sludge applied was 1260 and 1393 m. tons/ha, respectively.

Andersson and Nilsson (1972) also evaluated accumulations of trace elements in soils which had received prolonged application of sewage sludge. Their results cannot be compared to those of Le Riche (1968) because the method of extracting the trace elements from soil differed and amounts applied were considerably lower. Andersson and Nilsson (1972) determined trace elements extracted by 2 M HCl at 100C, except for Hg where 2 M HNO_3 was used. The changes which occurred in the trace element concentration of the surface 20 cm as reported by Andersson and Nilsson (1972) are presented in the first three columns of Table 30. The results show that the concentrations of B, Mo, Cd, Ni, Cr, Pb, and Se are increased by factors of 1.3-2.4 in the sludge-amended soils, Cu and Zn are increased by ~3.6 times and Hg by ~38 times. Although these rather large increases are observed in the sludge-amended soils, the concentrations for the treated soils are still within the range considered normal for soils (see Table 15). A linear log-log relationship between the log of the concentration of trace element in sludge and the log of the change in the concentration of trace element in soil was observed by Andersson and Nilsson (1972). The relationship, $\log \Delta C_{soil} = 1.06 \log C_{sludge} - 1.53$ showed a correlation coefficient (r) equal to 0.93.

Utilizing the data reported by Andersson and Nilsson (1972), it is possible to estimate the amount of trace elements applied in sludge which remains in the surface 20 cm of soil by making the following assumptions: (a) the trace element concentrations of the sewage sludge for each application were the same as those reported for a single year; (b) the bulk density of the soil in the surface 20 cm is uniform and equal to 1.33 g/cm^3. The percent recoveries of trace elements in the surface 20 cm, computed from the data of Andersson and Nilsson (1972) by making the above assumptions, are presented in Table 30. The results show more Zn, Ni, Cr, Pb, Cd, Hg, and Se recovered than were applied. This anomaly may be due to changes in the concentrations of trace elements of the sludges from one application to another, to an inaccurate estimate of the bulk density of the soil, or to sampling and analytical errors. Although the recovery estimates yield data which are questionable,

Table 30--Changes in the concentrations of trace elements in the surface 20 cm of soil following application of 84 m. tons of sewage sludge over a period of 12 years[1/]

Element	Control Soil	Treated Soil	Total Amt. Applied[2/]	Percent Recovery[3/]
	----------μg/g----------			%
Mn	476	480	11.8	98
Zn	97.9	368.8	154	146
Cu	25.5	90.5	61.9	104
Ni	28.2	43.3	2.78	140
Co	14.2	14.6	0.38	100
Cr	36.1	61.0	5.56	146
Pb	25.7	43.9	9.25	125
Cd	1.2	1.7	0.35	110
Hg	0.018	0.675	0.38	170
Mo	0.53	0.68	0.23	89
As	12.3	12.5	0.21	100
B	0.59	0.76	0.95	49[4/]
Se	0.238	0.569	0.23	121

1/ Data are derived from those published by Andersson and Nilsson (1972).

2/ Assuming the bulk density of the soil was 1.33. Except for boron, percent recovery is based upon concentrations extracted with 2 M mineral acids.

3/ Within the surface 20 cm of soil. Losses are due to plant removal, leaching, and possibly erosion.

4/ Refers to recovery of water soluble boron.

they suggest that substantial enrichment of As, Cu, Mn, Mo, Ni, Co, Cr, Pb, Cd, Hg, Se, and Zn will occur in the surface of soils where sludges containing these trace elements are applied. Results for B indicate that the water soluble form in the sludge is lost to the extent of about 50 percent from the surface 20 cm of soil. This is as expected since B exists as molecular boric acid, $B(OH)_3$, and as such is only slightly absorbed.

Trace Element Concentrations of Drainage Waters From Soils Following Applications of Sewage Sludge

In all studies discussed previously, no data are presented on the changes which may occur in trace element concentrations of soil solutions or drainage water from sludge-amended soils. The reason this seemingly important factor has been ignored may be related to difficulties in analytical determinations of the small concentrations of trace elements which occur in soil solutions.

Bradford (1973) has determined concentration of trace elements in soil solutions (saturation extracts) from fields irrigated with sewage treatment plant effluents and taken from the bottom of sewage sludge lagoons. A comparison of the concentrations of trace elements in the saturation extracts of the soils with those of the sludges applied is presented in Table 31. The data show substantial reductions in the concentrations of trace elements in saturation extracts of sludges once they are mixed with soil. However, generally speaking, concentrations of all trace elements in the sludge-amended soils exceed those commonly observed for saturation extracts from soils not treated with sewage sludges. But, with the exception of Cu, Ni, and Cd, the saturation extract trace element concentrations for the sludge-amended soils fall in the range reported for saturation extract concentrations of a wide variety of soils. (For data on the concentration of trace elements in a wide variety of soils see Table 8.)

Table 31--Trace element concentrations of saturation extracts from sewage sludge, soil taken from the bottom of sludge drying ponds (treatment plants A, B, C), and soil from effluent-irrigated fields (treatment plants D and E)[1/]

Element	Treatment Plant A		B		C		D		E	
	Sludge	Soil	Sludge	Soil	Sludge	Soil	Sludge	Soil	Sludge (NR)[2/]	Soil
	µg/ml									
Mo	0.10	0.01	0.23	0.04	0.11	0.05	0.10	0.01		0.04
Cu	0.14	0.09	1.6	0.25	1.1	0.23	0.14	0.05		0.75
Zn	0.5	0.11	1.0	0.27	1.5	0.10	0.5	0.04		0.4
Ni	18	2.0	0.6	0.09	0.18	0.07	18	0.30		0.05
Co	0.19	0.03	0.17	0.04	0.04	0.02	0.19	<0.01		0.02
Cr	-	0.40	-	0.01	0.01	0.01	-	<0.4		<0.01
Pb	2.0	0.22	0.3	0.06	0.13	0.05	2.0	0.06		0.17
V	0.04	0.03	0.05	0.04	0.10	0.03	0.04	0.01		0.06
B	2.7	0.40	4.4	2.0	6.0	0.66	2.7	0.6		0.5
Cd	1.2	1.2	0.09	<0.05	0.05	<0.05	1.2	0.40		<0.05
Ag	0.04	0.003	0.01	0.05	0.25	<0.002	0.04	0.002		<0.002

1/ From Bradford (1973). Soils sampled to a 15 cm depth.

2/ Not reported.

III. POTENTIAL IMPACT OF SLUDGE APPLICATIONS TO SOIL

The literature cited shows that trace element concentrations of sewage sludges vary from low to modest to extremely high. The evidence presented suggests that repeated applications of sludges high in Ni, Cu, or Zn to certain soils will produce toxicities to certain species of plants. Evidence is also presented which shows that productivity of soils can be maintained and possibly improved by modest applications of some sludges to soils for extended but not indefinite periods. Usually trace element toxicities to plants are more prevalent and acute where sludges are applied to acid soils. Also plant species exhibit rather marked differences in tolerance to levels of trace elements in sludge-amended soils. It thus appears that the amount of sludge which can be safely applied to soil, from a productivity point of view, will depend upon the composition of the sludge, the kind of soil to which it is applied, and the species of plant grown on the soil.

In addition to potential adverse effects on plant growth associated with trace elements in sludge-amended soils, the trace elements applied to soils may find their way into surface and subsurface water and thereby impair water quality. Also foods grown on sewage sludge-amended soils possibly could absorb trace elements in amounts sufficient to be hazardous to animals or humans who may consume them.

Chemical and Biological Transformations of Trace Elements in Sludge When Applied to Soil

Trace elements applied to soil, regardless of the form in which they are applied, may either pass through the soil unchanged, form insoluble or sparingly soluble inorganic and organic compounds, be sorbed by soil colloids as cations, anions, or molecules, be volatilized from the surface (Hg, As, Se) or be taken up by plants. Leeper (1972) recently presented a rather detailed review of the specific kinds of reactions which may occur when trace elements are applied to soil. The discussion which follows will be more general and attempt to point out the most probable transformations which occur based upon existing data and the author's experience.

Organic Trace Element Transformations

Under aerobic soil conditions, the organics in the sludge are microbially decomposed to CO_2 and H_2O or partially decomposed with products being incorporated into the humus fraction of soil. Under anaerobic conditions organics are incompletely metabolized. Organic acids, chiefly acetic and butyric, accumulate as end products. Methane and lesser amounts of hydrogen and other volatile products (sulfides) are evolved. The organic acids serve as substrates for bacteria. Under anaerobic conditions, microbial decomposition of organic matter present or added is much slower than under aerobic conditions. The microbial processes under both anaerobic and aerobic conditions are extremely complex and rates and intermediate products are dependent upon many soil environmental factors. The processes involved in the decomposition of organics added to soil from sewage sludge would be quite similar to those which occur with organics from other sources. Where sludges are incorporated into soils after decomposition had proceeded for a time, it would be impossible to distinquish between end products of organic matter added in sewage sludge and organics initially present or added from other sources.

Trace metals such as Cu, Ni, Co, Pb, Zn, Mn, and others exhibit rather high affinities for soil organic matter. More or less stable soluble and insoluble complexes between these elements and soil organic matter may form. The trace element-organic complexes have not been characterized in detail, but it is generally known that they involve binding of the trace element ion through principally carboxyl, phenolic, and imide functional groups in the organic matter. In situations where solubilities of trace elements exceed solubility products of inorganic compounds known or suspected to occur in soils, it is generally thought that the trace element exists in the soil solution as a soluble organic complex. Recent reviews of trace element organic complexes formed with soil organic matter and their relative stability constants have been published by Schnitzer and Khan (1972), and Stevenson and Ardakani (1972). Norvell (1972) also has recently evaluated soil systems

relative to competitive reactions between various ions and their organic complexes. Organics in sludge are somewhat similar to organics which are added to or occur in soils; thus it would appear that kinds of trace element organic complexes in sewage sludges may be similar to those which occur or may be formed in soil. Tan, King, and Morris (1971) present data which suggest that complexes formed between Zn and fulvic acid extracted from sewage sludge are similar to those formed with fulvic acid extracted from soil organic matter.

Inorganic Trace Element Transformations

The total concentration of trace elements in an organic form in sludges most probably undergoes microbial and chemical transformations once the sludge is incorporated into the soil. However, a sizeable percentage of the trace element concentration in sludge which occurs in an inorganic form may be quite stable, and remain essentially unchanged once the sludge is incorporated into the soil. To define inorganic reactions of sludge derived trace elements with soil requires knowledge of the chemical form of these elements in the sludge. Presently, our knowledge of chemical forms of trace elements in sewage sludge is nil.

Following incorporation of sludge into soil, the percentage of the total trace element concentration in the sludge in stable form will have a marked effect on subsequent chemical and biological reactions. Furthermore, the percentage of stable forms in sludges probably varies from one sewage treatment plant to another. Thus, for the same or similar soils, applications of different sludges having the same total trace element concentrations may not affect soil properties, water quality, plant growth, and availability to microorganisms and higher plants in the same manner. Inorganic stable solid phases of trace elements in soils have been characterized to some extent. Studies to characterize these inorganic forms in soils have involved mainly mineralogical and chemical analyses and solubility product considerations.

Studies on the solid inorganic phases which control the solubility of trace elements in soils have involved mainly solubility product

principals. Notable advances in our knowledge of the factors controlling the solubility of trace elements in soils and natural waters have been made recently. However, the subject is extremely complex and the science is not developed to the state that trace element solubilities in natural systems, including soils, can be predicted. Lindsay and his co-workers (Lindsay, 1972) have shown that concentration of Cu, Zn, and Mn in many soil solutions are less than those predicted from the solubility of the hydroxides and carbonates of these elements. Hem (1972) arrived at a similar conclusion regarding the concentrations of Zn and Cd which occur in surface and ground waters. Generally speaking, these recent works have served to eliminate several compounds from consideration as controlling factors in the solubility of trace elements in natural systems, but have not defined the specific compounds or surface reactions controlling solubilities.

The trace elements Mn, Ba, Cu, Zn, Ni, Cd, Co, and Pb, if not complexed with organic matter, most probably exist in soil solutions predominantly as divalent cations. Many other inorganic complex ions, molecules, and ion pairs of these elements are known to occur in equilibrium with the divalent form. These complex ions have the general formula $M_aX_b^{(2a-b)}$ where M is the divalent cation and X the anion. The complex can be cationic, neutral, or anionic. Examples of these kinds of naturally occurring complexes of Hg are listed on page 67. Knowledge of the equilibria between simple inorganic trace element ions and their complex forms, in most cases, is not developed to the extent that it can be applied to soil solutions.

Published data indicate that the concentrations of those trace elements which exist in solution as cations (Mn, Cu, Zn, Ni, Cd, Co, Sn, Cr, Pb, and Ag) usually occur in neutral (pH ~7) soil solutions at concentrations less than 0.05 µg/ml (Table 8). In acid soils (pH 5-6) concentrations in solution usually increase and in slightly alkaline and calcareous soils (pH 7.5-8.5) they usually decrease. In the pH range common to soils generally (pH 5-8.5), concentrations of the cationic trace elements do not exceed 0.25 µg/ml. The precise factors governing the solubilities of these trace elements in soil solutions

are not known. However, limiting values based upon solubilities of carbonate, hydroxide, and phosphate forms can be predicted. Generally, solubility product considerations would limit concentrations in solution to levels of 1 μg/ml or less. Under reducing conditions, sulfides of Mn, Cu, Zn, Ni, Cd, Co, Sn, Cu, and Pb could form. The sulfides of these trace elements are quite insoluble, so solubilities in anaerobic soils may be limited by sulfide precipitation. These generalizations and available published information demonstrate that cationic trace elements are quite immobile in most soils (possible exceptions are very acid soils, sandy and organic soils). These trace elements when applied to soil, regardless of the form, therefore will be retained largely in the surface soil to the depth of mixing (tillage).

The trace elements As, Mo, and Se occur in solution most commonly as divalent anions. Arsenic is chemically akin to phosphorus and its reactions in soils resemble those of phosphorus. In acid soil (pH <5.5) arsenate ($HAsO_4^{-2}$) reacts with active iron and aluminum, if present, and sparingly soluble iron and aluminum arsenates possibly control the concentrations of As in solution. In neutral and calcareous soils, arsenate reacts with calcium to form sparingly soluble calcium arsenates. The arsenates of calcium are more soluble than those of iron and aluminum. Consequently, As is usually more soluble in neutral and calcareous soils than in acid soils. In soils where active iron, aluminum, and calcium occur, As added to soil is most likely quite immobile and can accumulate; but in soils where little active iron, aluminum, or calcium occur, As applied could be leached to lower depths in soil profile.

The behavior of Mo and Se probably quite closely resembles that of As. Both trace elements are mobile in sandy soils devoid of organic matter and active iron, aluminum and calcium. Current evidence indicates that active iron and aluminum in acid soils limits the solubility of these elements in soil solutions. The elements become more soluble in neutral and calcareous soils, because calcium forms are more soluble than the iron and aluminum forms.

Boron, except in highly alkaline soils (pH > 8.5), occurs in soil solutions as undissociated boric acid [$B(OH)_3$]. It is sorbed by active

oxides of iron and aluminum in soil, but its affinity for these solid surfaces is low compared to affinities of other trace elements for surfaces in general. For these reasons B is quite mobile in soils. In sandy soils low in organic matter and active iron and aluminum oxides, B in waters passes through soils essentially unchanged. Organic matter and active iron and aluminum oxides tend to limit somewhat the mobility of B in soils, but generally the equilibrium involved is such that substantial percentages of the dissolved B remain in solution and as such are mobile in soil. Our knowledge of solubilities of boron in relation to soil organic matter contents is sparse; consequently, the generalization discussed may be subject to qualifications dependent upon organic matter contents.

Concentrations of Hg reported to occur in natural waters and soil solutions are usually less than 0.001 µg/ml (Lagerwerff, 1972, and Bradford, 1971). It may occur in solution as soluble elemental Hg, Hg_2Cl_2, $HgCl_2$, and $Hg(OH)_2$. In sea water, Bowen (1966) reports the dominant form of mercury as $HgCl_4^{-2}$. Under reducing conditions Hg may precipitate as HgS, which would limit its concentration to <0.002 µg/1. Mercury exhibits high affinity for humic substances, particularly those with S and SH function groups. It is also bound tightly to sediments such as hydrous oxides of iron and manganese. In surface soils Hg may be lost as volatile elemental Hg. Because of high affinity for humic substances and other inorganic constituents in soil, Hg is not expected to leach from many soils.

Evaluation of Criteria Available to Judge Feasibility of Sludge Applications

The principal problem associated with attempting to evaluate the potential impact of sewage sludge applications on soils' capacity to produce safe consumer crops and upon the quality of waters draining from soils is the lack of available information upon which one can base evaluations and recommendations. An analysis of the information currently available follows.

Soil and Plant Composition Criteria

Most research on trace elements in soils has been concerned with deficiencies rather than excesses. There are virtually no reliable soil tests available to diagnose trace element toxicities to plants. Those which have been discussed under "Results of Published Reports" serve to demonstrate the inadequacy of the methods currently used. A few plant analyses criteria for excesses of certain trace elements in soil have been developed (Table 15), but these are fragmentary and inadequate. They apply to "normal" soils and may not be applicable to sewage sludge-amended soils. Also, plant analysis techniques have the disadvantage that they indicate the problem after it exists, when what is needed is a technique to predict problems before they occur.

Another means of evaluating consequences of trace element contamination of soils resulting from sewage sludge additions is a comparison of the amounts of trace elements added to soil in the form of sludge with the maximum concentrations which normally occur naturally in productive soils. Although information is lacking to judge maximum concentrations of trace elements in soils which can be tolerated and still preserve soil productivity, trace element enrichment beyond normally maximum natural levels -- particularly within the root zone of the crops -- should be viewed as potentially damaging until information to the contrary is developed.

Water Quality Criteria

Sewage sludges are frequently applied to soil in a dilute suspension (up to 3%) usually utilizing sprinkler irrigation techniques. Under these conditions it may seem appropriate to evaluate sludge applications in this form in terms of quality criteria developed for irrigation waters. However, by doing this, unnecessary restrictions may be placed upon the use of liquid sewage sludges since criteria for irrigation waters are based upon solution as opposed to suspension concentrations.

In situations where sewage treatment plant effluents (waste waters as opposed to sludges) are used as supplemental or entire sources of

irrigation water, the water quality criteria developed for irrigation waters should provide interim guidelines upon which the feasibility of applying sewage treatment plant effluents to soils can be judged. Irrigation water quality criteria have been developed by the National Academy of Sciences (NAS) (1973), U. S. Department of Interior (USDI), Federal Water Pollution Control Administration (FWPCA) (1968), and state and regional water quality control boards. McKee and Wolf (1971) have reviewed state control board water quality criteria and standards. Water quality criteria for trace elements in irrigation waters developed by the NAS (1973) and the USDI (1968) are reproduced in Table 32. For reference, surface water standards which conform to the standards set by the U. S. Department of Health, Education, and Welfare for drinking waters (U. S. Dept. Health, Education, and Welfare, 1962) are also included in Table 32.

Consequences of Trace Element Enrichment in Sludge-Amended Soils

The review of the literature presented shows that information upon which one can judge specific consequences of trace element enrichment in sludge-amended soils is lacking. It is informative, however, to evaluate the consequences of sewage sludge applications to soils based upon what is currently known. In the discussion which follows, amounts of trace elements applied to soils will be compared to those normally present naturally. Consequences of trace elements in sludge-amended soils as they relate to productivity and quality of crops and water quality will also be evaluated.

Soil Enrichment

A hypothetical domestic sewage sludge was selected to evaluate trace element enrichment in sludge-amended soils in terms of normal concentrations naturally present. The trace element concentrations of this hypothetical sludge are presented in column 2 of Table 33. They represent the author's estimates and are based upon median concentrations and trace element concentration ratios obtained from analyses of a large number of sewage sludges.

Table 32--Surface and irrigation water quality criteria for trace elements

Element	Surface Water	Irrigation Water		
		Continuous Use		Short-Term Use
	FWPCA[1/]	FWPCA	NAS[2/]	FWPCA[3/]
		Any Soil	Coarse-Textured Soil	Fine-Textured Soil
	mg/l			
As	0.05	1.0	0.1	10
Ba	1.0	-	-	-
B	1.0	0.75	0.75	2.0
Cd	0.01	0.005	0.01	0.05
Co	-	0.2	0.05	10.0
Cr	0.05	5.0	0.1	20.0
Cu	1.0	0.2	0.2	5.0
Pb	0.05	5.0	5.0	20.0
Mn	0.05	2.0	0.2	20.0
Mo	-	0.005	0.01	0.05
Ni	-	0.5	0.2	2.0
Se	0.01	0.05	0.02	0.05
V	-	10.0	0.1	10.0
Zn	5.0	5.0	2.0	10.0
Ag	0.05	-	-	-

1/ U.S. Dept. of Interior, Federal Water Pollution Control Administration (1968). Surface water criteria are virtually the same as drinking water standards (U.S. Dept. of Health, Education, and Welfare (1962).

2/ National Academy of Sciences (1973). Recommended maximum concentrations of trace elements in irrigation waters used for sensitive crops on soils with low capacities to retain these elements in unavailable forms.

3/ For short-term use only on fine-textured soils.

Table 33--Comparison of amounts of trace elements added to soil to a depth of 15 cm from 100 m. tons of a typical domestic sewage sludge with amounts commonly present

Element	Conc. in Sludge[1]	Amt. Applied to Soil[2]	Amt. Present in Soil (kg/ha)[3]	
			Normal Range	Typical Level
	µg/g	kg/ha		
Ag	10	1	0.02-10	0.2
As	5	0.5	0.2 -80	12
B	50	5	4 -200	20
Ba	1000	100	200 -6000	1000
Cd	10	1	0.2 -1.4	0.12
Co	10	1	2 -80	16
Cr	200	20	10 -6000	200
Cu	500	50	4 -200	40
Hg	5	0.5	0.02-0.6	0.06
Mn	500	50	200 -8000	1700
Mo	5	0.5	0.4 -10	4
Ni	50	5	20 -2000	80
Pb	500	50	4 -400	20
Se[4]	1	0.1	0.02-4	0.4
Sn	100	10	4 -400	20
V	50	5	40 -1000	200
Zn	2000	200	20 -600	100

1/ Based upon information presented in Tables 1, 2, 3, and 5.

2/ Assuming the sludge is mixed to a depth of 15 cm and the bulk density of the soil is 1.33 g/cm^3.

3/ Derived from data reported by Bowen (1966).

4/ The Se concentration of the sludge is based upon an estimated from the content in municipal solid waste as reported by Johnson (1970).

Since applications of sludge are made on the basis of an amount applied to a unit area and concentrations in soil are expressed on a weight basis, to make comparisons it is necessary to assume that the amount of trace elements applied in sludge to the surface will occupy a certain volume of soil. If it is assumed that the sludge is incorporated to the depth of tillage (~0.15 m) the volume of soil in one hectare is 1500 m^3. By specifying a bulk density for the soil of 1330 kg/m^3 (an average value for many textural classes of soils) results of soil analyses expressed in units of mg element per kg soil (ppm) can be converted to units of kg/ha. Table 33 shows the amount of trace elements added to the surface 0.15 m of soil from the application of 100 m. tons of the hypothetical domestic sludge per hectare and compares them with amounts of trace elements commonly found in untreated soils. The rationale behind using a rate of 100 m. tons/ha is that it is a convenient figure from which one can extrapolate to other application rates, and it represents a low application rate of 10 m. tons per hectare per year for a period of 10 years. This annual application rate approximates that recommended in Sweden (Andersson and Nilsson, 1972).

The data show that 100 m. tons of typical domestic sludge per hectare (45 s. tons/acre) will add more Zn, Cu, Pb, Cd, Hg, and Ag to the surface 15 cm than is typically present (Table 33). However, the amounts added plus amounts initially present fall within the normal range for many soils. The available evidence indicates that trace elements applied to most soils are retained in high percentages to the depth increment of tillage. Management practices involving deep tillage will serve to reduce concentrations in the surface by mixing with a larger volume of soil. Thus, employing practices which mix the applied sludge to greater depths in soil will tend to proportionately increase the total amount of sludge which can be applied before typical concentrations of unamended soils are exceeded. The data, therefore, indicate that domestic sludges (only slight industrial inputs) could be applied to soils for a number of years at rates of 10-20 m. tons/ha and not cause trace element concentrations uncommon to soils in general. Sewage sludges from metropolitan areas with large industrial inputs contain considerably

higher concentrations of many trace elements than those listed in Table 33. Each should be evaluated independently to determine the extent to which soils would be enriched with trace elements by their application.

Cadmium, Copper, and Zinc. These three elements have been grouped together since their chemistry is somewhat similar and they commonly occur in many sludges at concentrations which exceed those normally found in soil.

As mentioned previously, the data presented in Table 33 show that application of 100 m. tons/ha of a typical domestic sludge if mixed uniformly throughout the surface 15 cm would add more Cd, Cu, and Zn than is typically present in this zone. The Cd concentrations in natural soils are quite low; consequently, even modest applications of sludge containing a few mg Cd/kg if applied for a decade or so would enrich the surface 15 cm of soil to levels beyond those typically observed naturally. The range of normal values for Cd (0.2-1.4 kg/ha) in soil is considerably less than the normal range for Cu (4-200 kg/ha) and Zn (20-600 kg/ha). The maximum values in the normal range for Cu and Zn in natural soils would be exceeded in the surface 15 cm by applications of the typical sludge equal to 400 and 300 m. tons/ha, respectively. For Cd, the maximum value in the normal range would be exceeded by an application of 140 m. tons/ha.

Lead and Mercury. Application of 100 m. tons of the typical domestic sludge would also add more Pb and Hg to the surface 15 cm of soil than is typically present (Table 33). In the case of Hg, the amount applied in 100 m. tons of sludge is considerably greater than that typically present, and approaches the maximum soil level in the normal range. An application of 120 m. tons/ha of the typical sludge would yield concentrations of Hg in the surface 15 cm equal to the maximum level observed in the normal range for untreated soils. With Pb an application of 800 m. tons/ha could be tolerated before the maximum concentration in the normal range for unamended soils was reached.

Nickel and Chromium. Concentrations of Cr and Ni in the typical domestic sludge are such that applications of 1000 and 1600 m. tons/ha would be required to produce concentrations in soil which would exceed those typically present in natural soils (Table 33). It would appear from the approximations made that sludge enrichment of other trace elements in soil, namely Hg, Cd, Zn, and Cu in that order, may become limiting relative to potential hazardous concentration before Ni and Cr could present problems. However, sludges from metropolitan areas with large industrial inputs may contain concentrations of both Ni and Cr considerably in excess of those found in domestic sludges. Concentrations of a few thousand mg/kg and even greater are not uncommon in industrial sludges. Thus, although Ni and Cr may not become controlling factors in limiting amounts of domestic sludge applied to soil, they may do so in the case of industrial and metropolitan sludges.

Arsenic, Molybdenum, and Selenium. Concentrations of Se common to natural soils are somewhat less than those of Mo and As. Representative concentrations for Se in sludge are rather difficult to deduce from the published literature because of the very limited number of analyses available. The concentration used for the hypothetical sludge was estimated from data reported for municipal solid waste by Johnson (1970). Andersson and Nilsson (1972) report a value of 7.3 μg/g in sludge from Sweden. Using Johnson's data as representative of a domestic sludge indicates that applications of 400 m. tons of domestic sludge per hectare could be tolerated before the typical level of Se for natural soils would be exceeded. In the cases of Mo and As, sufficient data are available to make what the author considers reasonable estimates for their concentrations in sludge. The data in Table 33 show that 800 m. tons/ha of domestic sludge would be required to produce concentration levels in soils equal to those observed naturally for Mo. Applications of 2000 and 4000 m. tons of domestic sludge per hectare would produce concentrations of Mo and Se in excess of the maximum concentrations normally observed for natural soils. Excessive enrichment of soils with As by domestic sludge applications appears improbable (Table 33).

Boron. Boron occurs in both organic and inorganic form in soils. In inorganic form in soil solutions, it occurs as undissociated boric acid. As such it is not retained by soils to the degree of the other trace elements discussed. Current evidence indicates that soils have little capacity to retain B in an inert form and that high percentages of applied B will move with water to lower depths in the profile. Therefore, the data contained in Table 33 overestimate concentrations of B in the surface 15 cm of soil. They show that application of 400 m. tons of domestic sludge per hectare would yield a concentration in the surface 15 cm equal to a typical level for natural soils.

Barium, Cobalt, and Vanadium. Very little direct information is available on the chemistry of these elements in natural soils. The data presented in Table 33 show that domestic sludge applications in excess of 1000 m. tons/ha would be required to produce concentrations of Ba, Co, and V in the surface 15 cm of soil in excess of those typically present in natural soils. To reach maximum concentrations in the normal range of natural soils would require unrealistically high additions of sludge. Thus, it appears that these three elements can be removed from consideration as limiting relative-to-excessive trace element enrichment in soils from domestic sludge applications.

Silver and Tin. The estimated concentration of Ag in the hypothetical domestic sludge given in Table 33 is based upon less extensive sludge analyses than are concentrations of the other trace elements (except for Se). It was derived from data presented by Berrow and Webber (1972). Typical concentrations of Ag in soils are quite low, so as with Cd, Hg, and Se, modest applications of domestic sludges containing a few μg Ag/g will enrich soils beyond concentrations normally naturally present (Table 33). Silver should be relatively immobile in soils since it is adsorbed by soil minerals, and forms sparingly soluble chloride, carbonate, and other salts.

Concentrations of Sn in domestic sludge are such that 200 m. tons/ha would produce concentrations in soil equal to typical levels for natural soils. To reach the maximum level in the normal range for natural soils, however, would require an application of 4000 m. tons/ha

domestic sludge. Tin is generally thought to be quite inert in soils (Wallihan, 1966). It is unlikely to be damaging when applied to soil in the form of domestic sludge.

Manganese. Unrealistically high amounts of domestic sludge would be required to enrich soils beyond the normal maximum concentrations which occur naturally (Table 33).

Crop Productivity and Quality

The literature reviewed indicates that sewage sludges from most sewage treatment plants can be applied in modest amounts to most soils for limited periods of time without causing trace element toxicities or adversely affecting the quality of most crop species. Continued applications of most sewage sludges for long period of time (decades), however, will probably adversely affect plant growth due to trace element soil enrichment and subsequent plant toxicity. The trace element composition of the sludge will determine the total amounts which can be applied to soils over a period of years before adverse effects on crop yields and possibly quality will occur.

Crop Productivity. It is difficult to generalize about the effects of trace element enrichment of soils on crop productivity. Trace element interactions which are dependent upon chemical properties of soils may indirectly affect plant growth. Plant species exhibit natural variability and vary markedly in their tolerance to concentrations of trace elements in soil. Thus, yields of sensitive crops may be drastically reduced by a particular level of sludge application where yields of tolerant crops would be unaffected. A detailed treatise of tolerances to trace elements for a wide variety of plant species is presented by Chapman (1966).

The data published suggest that continued applications of sludge could produce concentrations of trace elements in soil which may increase or decrease plant growth. Trace elements in sewage sludge could serve as a source of plant essential trace elements where they are either naturally deficient or present in a plant unavailable form in soil. Studies have shown that most trace elements are toxic to higher plants if they occur in soil solutions in excessive amounts (Pratt, 1973). Of

those trace elements considered in the present review, it appears that concentrations of Ag, Mo, Hg, and Sn in all sludges are such that yield reductions caused by toxicities of these elements in sludge-amended soils are unlikely. With domestic sludges (small industrial input) toxicities to higher plants caused by buildup of As, Ba, Co, Cr, Mn, and V are unlikely. Those most likely to cause toxicities to higher plants in soils to which large amounts of domestic sludge are applied over a period of years are B, Cd, Cu, Zn, and possibly Ni, Pb, and Se. With respect to Cd, Cu, Zn, Pb, and Ni toxicities would probably occur at lower concentrations and be more acute in acid soils. Concentrations of As, B, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, V, and Zn may be sufficiently high in certain sludges from highly industrialized areas to cause yield reductions of crops when applied in copious amounts to agricultural land. Sludges from highly industrialized areas must be considered independently because their trace element concentrations are so highly variable.

Quality of Crops. Quality considerations will be restricted to those associated with accumulations of trace elements in plants which produce metabolic imbalances or toxicities to man and animals. Only a limited number of references to illustrate points discussed are cited. More complete reviews on the subject are presented by McKee and Wolf (1971), Lisk (1972), Allaway (1968), and Scott (1972).

Feed and food plants can grow at normal or near normal rates and still contain sufficient Se, Cd, Mo, and possibly Pb to cause either direct toxicity or metabolic imbalance in animals that consume these crops (Allaway, 1968). Other plants, however, may grow normally but contain insufficient concentrations of Co, Cr, Cu, Mn, Se, and Zn to meet the dietary requirements of animals. Thus, with respect to certain trace elements added to soil in the form of sludge, the quality of feeds and foods could under certain conditions be improved, while under others detrimental effects may be encountered.

Selenium. Selenium is essential in the diet of livestock at low concentrations but toxic at higher concentrations. Soils from widespread regions throughout the United States produce forage without sufficient Se to satisfy the dietary requirement of animals (Kubota

and Allaway, 1972). In other regions, Se concentrations in soils are sufficiently high to produce forage containing concentrations of Se which are toxic to animals (Ganje, 1966). The range between dietary deficiency and toxicity is quite narrow. According to Allaway (1968), concentrations of Se required in the diets of various animals to prevent Se deficiency range from 0.04-0.20 μg Se/g depending upon the kind of animal and the type of diet. Concentrations in excess of 4-5 μg/g are toxic to animals. Allaway (1968) suggests that it would be desirable to control the level of Se in food and feed crops somewhere between 0.1-1.0 μg/g. Selenium added to soil as selenized superphosphate or barium selenate at rates of approximately 2 kg/ha produced toxic levels of Se in the first few cuttings of alfalfa (Cary, **Wieczorek,** and Allaway, 1967; Carter, Brown, and Robbins, 1969). Very little information is available on concentrations of Se in sewage sludge. The above information suggests that if Se were to occur in sewage sludge at concentrations greater than a few μg/g, and if it were applied to soil for a number of years, the concentration of Se in soil could build up to the extent that forage might absorb sufficient amounts to be toxic to animals.

Molybdenum. Molybdenum, like Se, is an essential element for animals at low concentrations but is toxic at higher concentrations (Allaway, 1968). Toxic concentrations of Mo are related to the level of Cu and SO_4 in the diet. Where Cu is low in the diet, concentrations of Mo in forage as low as 5 μg/g may cause a disorder in animals called molybdenosis or molybdenum-induced copper deficiency. Ruminant animals are more susceptible to molybdenosis than are nonruminants. Sewage sludges contain Mo, so depending upon the concentration in the sludge and the amount applied, it is possible that soils could become enriched to the extent that plants would absorb quantities of Mo sufficient to be toxic to animals. Both Mo and Se are more plant-available in neutral and alkaline soils than in acid soils. In this respect, Mo and Se are unique, since they are potentially more damaging in neutral soils, while the other trace elements are potentially more damaging in acid soils.

Cadmium. Studies in Japan (Yamagata and Shigematsu, 1970), the U.S.A. (Schroeder, 1971), and Sweden (Friberg, **Piscator,** and Nordberg, 1971) show that chronic exposure to Cd may result in accumulation of

levels in man and animals which will cause a serious decline of health and even death. The Japanese studies (Yamagata and Shigematsu, 1970) particularly have demonstrated that foods cultured on Cd-polluted soils irrigated with Cd-polluted waters can accumulate sufficient Cd to be hazardous to human beings who consume these foods.

Recent data accumulated by a number of workers (John, Chuah, and Van Laerhoven, 1972; John, 1973; Page, Bingham, and Nelson, 1972; Haghiri, 1973) show that certain crops accumulate excessive amounts of Cd from substrates treated with Cd from inorganic sources. Bingham et al. (1973) present data which show that the leafy portion of plants grown on soils to which Cd-fortified sewage sludge was applied accumulates substantial amounts of Cd. Although regulatory agencies have not set levels for maximum dietary intake of Cd, the current information indicates that certain foods, if grown on Cd-contaminated soils, will accumulate amounts of Cd which are potentially hazardous to human and animal health.

Sewage sludges, particularly those from metropolitan areas, may contain rather high concentrations of Cd. If these sludges are applied to soil in modest amounts for a number of years, the Cd concentrations in soil could become large enough to produce concentrations in foods grown on the soils which may be toxic. Certain workers (Leeper, 1972; and Chaney, 1973) suggest that it is not the Cd concentration in soil "per se" which determines Cd accumulation by plants. They suggest that the Zn:Cd ratio in the substrate will determine amounts of Cd absorbed by plants. Chaney (1973) indicates that as long as this ratio (Zn:Cd) is 200 or greater, foods will not accumulate hazardous concentrations of Cd. The subject is complex and additional research is needed to resolve potential hazards associated with the Cd-Zn-soil-plant system.

Lead. Lead poisoning of animals and humans caused by excessive amounts of Pb in foods and beverages consumed, and in air, is well documented (National Research Council, 1971; Zimdahl and Arvek, 1973). In those instances where Pb toxicities to animals and humans have occurred, the sources of Pb in the foods and feeds were not due to plant absorption from soils but were caused by contamination during

processing, storage, or deposition from lead in air onto plant surfaces. The principal source of Pb in air is the combustion of leaded gasoline by motor vehicles. As far as the author is aware, there are no known occurrences of Pb poisoning caused by feed and foods absorbing excessive amounts of Pb from soil.

Sewage sludges may contain rather large quantities of Pb. The information available indicates that crops absorb relatively small amounts of Pb when grown on lead-contaminated soils. Except possibly in certain unique and isolated instances, it is doubtful that sludge applications to soils will result in enrichment in Pb to the extent that plants will accumulate hazardous concentrations.

Water Quality

In terms of trace element composition the quality of waters resulting from sewage sludge applications to soils can be evaluated with respect to (a) the composition of the solution as it moves through the soil profile and strata below and (b) the composition of surface drainage water.

The data reviewed show that the concentrations of dissolved trace elements, except possibly for B, are reduced once the sludge comes in contact with soil; the extent of reduction is dependent upon soil chemical properties. Generally, the capacities of coarse textured (sandy) soils to reduce trace element solution concentrations of the applied sludge are less than those of fine textured (clayey) soils. The extent to which the soluble trace elements in sludge are reduced is also dependent upon the soil pH. Except for As, Mo, Se, and B, trace elements are more soluble in acid than neutral soils. Solubilities of As, Mo, and Se increase slightly with increased soil pH. The solubility of B is more or less independent of soil pH. Therefore, with respect to trace elements, except possibly for B, soils have a capacity to "purify" waste waters.

The trace element composition of soil solutions from sludge-amended soils should progressively decrease as the depth of percolation within the soil increases until a composition characteristic of the natural soil is reached. Data reported by Bradford (1973) (Table 31) show that the concentrations of Cu, Ni, B, Cr, Mo, and Cd in soil solutions obtained

from sludge-amended surface soils are greater than those considered safe for irrigation use (compare data in Table 31 with those in Table 32). To correct this situation sludge applications could be discontinued and the soil could be leached with waters which meet the minimum recommended concentrations for irrigation waters (Table 32). This practice should displace the trace element-contaminated soil solution to lower depths in the soil profile and thereby expose it to more soil and reduce solution concentrations of the trace elements. Information on the movement of trace elements within soil profiles is meager. Consequently, critical evaluations of trace element composition of sludge-amended soils in relation to depth in soil profiles are not possible at the present time.

The extent to which underground water supplies may become contaminated with trace elements from sludges applied to soil is largely dependent upon the soil's chemical properties and the distance the percolating solution must move through the soil to the water table. The potential for trace element contamination would be greatest where shallow water tables (a few meters) occurred beneath sandy low organic matter soils. Conversely, where the water table occurs at great distances from the surface (100 meters) the probability of trace element contamination of underground water is essentially nil. Of those trace elements considered in this paper, boron would move in both soil profiles and the strata below at the greatest rate. Movement of Ba, Cd, Co, Cr, Cu, Pb, Mn, Ni, Zn, and Ag should be least; Mo, As, and Se should move at a rate intermediate between B and the cationic trace elements. Pratt (1972) has developed techniques to compute transit times for drainage water movement in the unsaturated zone beneath the root zone of crops. Utilizing the concept of transit time in conjunction with other data, he was able to predict time lags associated with movement of nitrates in the alluvial materials of a particular basin. An approach similar to that used by Pratt (1972) may be feasible to predict the time required for B, and possible other trace elements, to move from the surface through an unsaturated zone to the ground water.

Since trace elements applied to soil are largely concentrated in the surface, drainage from surface soils into surface waters may contribute to trace element contamination of these waters. Concentrations of trace elements in water considered to be toxic to aquatic organisms are, in many cases, less than those considered to be toxic to animals, man, and higher plants. **Wilber** (1969) has reviewed trace element tolerances of aquatic organisms. Concentrations of Ag, Cd, Cr, Cu, Hg, Mo, Ni, and Pb as low as 0.01 μg/ml may have serious deleterious effects on certain species of aquatic life. Since these tolerances are so low, where sludges are applied to soils, surface runoff of either sediment or solution into surface water should not be permitted.

IV. SUMMARY

Concentrations of trace elements in sewage sludges are related to industrial and consumer uses. Uses of As, Ba, B, Cd, Cr, Co, Cu, Pb, Mn, Hg, Mo, Ni, Se, Ag, Sn, V, and Zn are briefly reviewed.

Total concentrations of trace elements in sewage sludges vary widely. The ranges reported for sludges from approximately 300 treatment plants from different regions in the U.S.A., Canada, Sweden, England and Wales were as follows (in μg/g dry matter): Ag (5-150), As (1-18), B (6-1000), Ba (150-4000), Cd (1-1500), Co (2-260), Cr (20-40,615), Cu (52-11,700), Hg (0.1-56), Mn (60-3861), Mo (2-1000), Ni (10-5300), Pb (15-26,000), Sn (40-700), V (20-400), and Zn (72-49,000). Selenium concentrations of sewage sludge are difficult to deduce from published literature because of the limited number of analyses available. Where excessive concentrations of one or more trace elements occur in sewage sludges, the source is probably industrial input. Sludges from strictly residential communities commonly contain concentrations of Cu in excess of 500 μg/g dry matter and Zn in excess of 1000 μg/g dry matter. The source of Cu and Zn in residential sludges is most likely contamination from metal pipes and tanks during conveyance, storage, or treatment.

Trace elements in sludges dissolved by acetic and citric acids and water vary markedly. No apparent relationship exists between the total concentration of trace elements in sludge and the amount dissolved by organic acids or water. This indicates that chemical forms of trace elements in sludges differ among sludges from different treatment plants. Trace element concentrations in the aqueous phase of sludges may exceed those predicted from solubility product considerations indicating that soluble trace element-organic complexes occur in liquid sludges.

Field and greenhouse studies have demonstrated that yields and trace element concentrations of higher plants grown on sludge-amended soils are dependent upon the amount of sludge applied, trace element composition of the sludge, soil pH, and plant species. Leeks, beets, potatoes, and carrots grew well on a particular soil which had received annual applications of sludge (66 m. tons/ha) for as long as 19 years. Although growth was not adversely affected, the tops of plants grown on sludge-amended soil absorbed more Cu, Zn, and Ni than tops of plants

grown on the control soil. Corn plants grown on field soils which received a total of 166 metric tons of sludge per hectare over a 3-year period grew well and did not absorb significant concentrations of Cr, Cu, Pb, Ni, and Hg. Concentrations of Mn, Zn, Cd, and B in corn leaves and Zn and Cd in corn grain were significantly increased by the sludge applications. Where 105 metric tons of sludge per hectare were applied to a field soil over a period of 15 years, yield of fodder rape was unaffected and only the concentrations of Zn in the plant tissue was increased substantially.

Where sewage sludges have been applied to acid soils (pH < 5.5) reports in the literature suggest that certain plant species are damaged by excessive concentrations of available Zn, Cu, or Ni in the soil. Oat plants were severely damaged when grown on an acid soil (pH 5.3) treated with 134 m. tons/ha of sludge, but in the same soil similarly treated with sludge and adjusted to pH 6.8 yield was unaffected. The sludge applied was unusually high in Ni (6480 µg/g dry matter) and growth depression in the acid soil was diagnosed as Ni toxicity. Nickel absorption by oat plants was decreased by increasing the soil pH. Yields of rye plants grown on an acid soil which was treated with sewage sludge at rates of up to 121 m. tons/ha were significantly reduced. Liming the soil to increase soil pH restored yields to levels near those of the controls. Concentrations of Zn in rye increased in relation to sludge application rate, but the increases were more profound in plants grown on the acid soils. At the higher application rates on the acid soils, Zn levels in the plant tissue were greater than those considered to be toxic to many plant species.

In most soils (exceptions are sandy or very acid soils) the percentage of Ag, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sn, and Zn applied in the form of sludge which moves beyond the depth of tillage is quite small. Mobility of Mo, As, and Se is also normally quite limited, but probably exceeds that of the cationic trace elements, particularly in neutral and alkaline soils. Boron is quite mobile in most soils and the available information indicates that high percentages of that applied in the form of sludge will move with water through the

soil profile. Sludges applied to soils may, therefore, contribute to B contamination of underground water supplies. Barium, Cd, Co, Cr, Cu, Pb, Mn, Ni, Zn, Ag, Mo, As, and Se are quite immobile in most soils and contamination of deep underground water supplies is unlikely. Where shallow water tables occur beneath sandy soils, the potential for trace element contamination of underground water supplies from surface applications of sludge is greatest. Since trace elements are concentrated in the surface of soil, sediment and solution runoff from sludge-amended soils could contribute to contamination of surface waters.

Published data show that the surface horizons of sludge-amended soils are enriched in trace elements. The extent of enrichment is dependent upon the amount of sludge applied and the trace element composition of the sludge. Applications of most any sludge equal to 400 m. tons/ha, if mixed uniformly throughout the surface 15 cm, will add more Cd, Cu, Hg, and Zn to this zone than is normally present in natural soils.

Molybdenum and Se are absorbed by certain forage crops in amounts sufficient to cause toxicities to livestock which consume these forages. Sewage sludges contain both Mo and Se so depending upon the concentration in the sludge and the amount applied, it is possible that soils could become enriched to the extent that forage crops would absorb quantities of Mo and Se sufficient to be toxic to livestock. Current information also indicates that certain foods, if grown on Cd contaminated soils, will accumulate amounts of Cd which are potentially hazardous to humans and animals. Sewage sludges, particularly those from industrial and metropolitan areas, may contain rather high amounts of Cd. If these sludges are applied to soils in modest amounts for a number of years, the Cd concentrations in soil could become large enough to produce concentrations in foods grown on the soils which may be toxic.

V. RECOMMENDATIONS FOR FUTURE RESEARCH

1. Fertility of many agricultural soils can be maintained and possibly improved by finite applications of most sewage sludges, but in time applications of sewage sludges will produce concentrations of trace elements in soils which will adversely affect crop productivity, quality, and possibly the quality of surface and subsurface waters. The current need is to develop the information necessary to predict the number of years sludges can be safely applied at modest rates to agricultural soils. This information needs to be developed for a variety of soils in various climatic regions and with a variety of plant species.

2. Diagnostic techniques to predict trace element tolerances of a variety of plants in relation to trace element concentrations in sludge-amended soils need to be developed.

3. Feeds and forages accumulate amounts of Mo and Se which are toxic to animals which consume them. Cadmium is also absorbed by foods in amounts which may adversely affect the health of humans and animals. The conditions under which these elements, and possibly other toxic elements, are absorbed by plants grown in sludge-amended soils need to be determined. Also research designed to select and breed plant varieties for tolerance to and exclusion of toxic trace elements should be initiated.

4. The manner in which climate may affect plant tolerances to and accumulations of trace elements in sludge-amended soils needs to be determined.

5. The effect of trace elements in sludge-amended soils on metabolic processes and nutritional quality of plants should be investigated.

6. Sewage sludges should be characterized to determine the chemical form of the trace elements which occur. Studies should be designed to determine the fate of trace elements in sludge-amended soils in relation to the form in which they occur in sludge. These studies should include the identification of chemical compounds and their solubility. Considerations should be given to ionic species in

solution, as well as total concentrations. Organic matter-trace element studies should identify stable organic soluble and insoluble complexes. The effect of soil parameters such as redox potentials, pH, and mineral composition on solubility and immobilization of trace elements in sludge-amended soils should be examined.

7. Because trace elements may be quite hazardous in minute amounts, "leakage" of even traces from soils could lead to surface and subsurface water pollution. The movement and distribution of trace elements in sludge-amended soil profiles in relation to soil chemical and physical properties need to be determined. These studies should be designed to identify soluble and insoluble forms which are retained in soils and strata above the water table, to establish the rate of movement to underground aquifers and water supplies in relation to soil properties, and to determine the conditions under which trace elements are removed from sludge-amended soils by erosion and volatilization.

8. The influence of trace elements in sludge-amended soils on microbial populations, activity, and processes should be evaluated.

9. Published data suggest that the response of a particular trace element in soil will depend upon the concentrations and kinds of other trace elements as well as other elements present in the substrate. Since sludges contain a variety of trace elements in concentration ratios different from those in natural soils, studies designed to evaluate the effects of trace element interactions on soil chemical properties, plant response and composition are needed.

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